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MILITARY FUELS REFINED FROM PARAHO-II SHALE OIL

INTERIM REPORT AFLRL No. 131

by

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Under Contract to

U.S. Army Mobility Equipment Research and Development Command Fort Belvoir, Virginia

Contract No. DAAK70-80-C-0001

Approved for public release; distribution unlimited

March 1981

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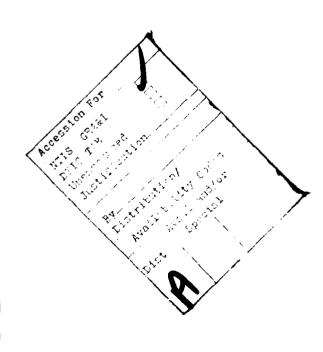
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20. ABSTRACT (cont'd)

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SUMMARY

During 1978 and 1979, a DOD/DOE joint project, with the Navy having the lead role, resulted in the refining at the Standard Oil Company (Ohio), Toledo Refinery of approximately 88,000 barrels of the shale oil produced by the Paraho retort process, into several fuels meeting military specifications. The products were JP-5, JP-8, marine diesel fuel (DFM), and residual fuel oil. Samples of these products were made available at the Army Fuels and Lubricants Research Laboratory for analyses and evaluation in a turbine engine combustor and diesel engines typical of those available in the U.S. Army inventory. This evaluation program was intended to ascertain the performance of these fuels in Army engine systems as part of the overall program within DOD to develop a capability for consuming multisource mobility fuels. The combustor is based on hardware from the Allison T-63 turbine engine used in several Army helicopters. The diesel engines employed were the Detroit Diesel 3-53 and 6V-53T, and the Continental LDT-465-1C and a single cylinder from the Continental AVDS 1790-2C, mounted on a CUE universal crankcase.

The analytical results indicate the fuels met virtually all the military specifications with the exception of the failure of the JP-5 to meet the copper corrosion requirement and the DFM to meet the maximum limit for pour point. A 32-week, 43°C storage test on these fuels indicated their storage stability was equivalent to that of petroleum products under these conditions. Accelerated stability tests at 80° and 150°C indicated instability at the lower temperature but none at 150°C. Compatibility studies of the JP-5 and DFM with petroleum-derived fuels, which consisted of accelerated stability tests at 80° and 150°C, indicated that the fuels studied are compatible with each other. The JP-5 and DFM responded to the addition of a cetane improver additive in a manner similar to that of a petroleum-derived material. The addition of an additive package developed for petroleum-derived fuels which contains a corrosion inhibitor incrementally improved the corrosion tendencies of the JP-5 and DFM but did not affect the JP-8. Microbiological growth susceptibility investigations conducted at the U.S. Army Natick Laboratories showed that growth of Cladosporium resinae was supported by the shale-derived JP-5 and DFM.

The performances of shale fuels in a turbine combustor were virtually analogous to that of a petroleum-derived fuel with respect to combustion efficiency, CO, NO, and unburned hydrocarbon emissions. Higher flame radiation and exhaust smoke levels were observed for the shale-derived JP-5 and DFM than were observed for a petroleum Jet A. The differences observed were attributed to the lower hydrogen content of the shale fuels.

Four diesel engines were used to compare the performance of shale-derived JP-5 and DFM with similar petroleum-derived products. In three engines the maximum power output and specific fuel consumption were compared and the only observable differences between the fuels were those attributed to differences in heat of combustion. A 210-hour endurance test was conducted using shale DFM. The results showed no power loss during the test nor evidence of distress or impending component failure; and piston deposits and component wear were acceptable. The performance results of the DFM in this endurance test were indistinguishable from those obtained with conventional petroleum-derived diesel fuel with similar properties.

FOREWORD

This work was conducted at the U.S. Army Fuels and Lubricants Research Laboratory (USAFLRL) located at Southwest Research Institute, San Antonio, Texas under Contracts DAAK70-78-C-0001 and DAAK70-80-C-0001 during the period June 1979 through November 1980. The work was funded by the U.S. Army Mobility Equipment Research and Development Command (MERADCOM), Ft. Belvoir, Virginia, with Mr. F.W. Schaekel (DRDME-GL) serving as contract monitor. Project technical monitor was Mr. M.E. LePera, MERADCOM-DRDME-GL.

A portion of this work was funded by the U.S. Department of Energy, Bartles-ville Energy Technology Center, under Contract EY-77-A-02-4162. Dr. D.W. Brinkman served as Technical Project Officer. Microbiological growth tests were conducted by U.S. Army Natick Laboratories.

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I. INTRODUCTION

The prospects of an energy shortage in the United States and continued reliance on imports of crude oil have prompted initiation of numerous projects with the objective of producing liquid fuels from sources other than conventional petroleum crude oils. Among natural resources that exist in great abundance in the U.S. and which can be converted into liquid hydrocarbon fuels are coal and oil shale. A third resource that exists in lesser quantities is tar sands. Recovering oil from shale and refining that oil into finished fuels appears to be the most readily available technology for the production of synfuels meeting current specifications.

In a recent joint Department of Defense/Department of Energy project managed by the Navy, 88,000 barrels of crude shale oil were refined into several thousand barrels of military fuels. ($\underline{1}$)* Drum quantities of JP-5 aircraft turbine fuel and marine diesel fuel (DFM), and less than drum quantities of JP-8 aircraft turbine fuel, were supplied to the U.S. Army Fuels and Lubricants Research Laboratory (AFLRL) for evaluation.

The purpose of the program was to evaluate the JP-5, JP-8, and DFM produced from the Paraho-II shale oil for specification requirements and other properties not necessarily defined by specification testing, and to ascertain their performance in Army engine systems as part of the overall program to develop a capability for consuming multisource fuels within the Department of Defense. The fuels were analyzed and compared to specification requirements, and additional analyses were performed to better define the components of these fuels and determine their storage stability, additive response, and compatibility with petroleum-derived fuels. The combustion performance was evaluated in a combustor based on hardware from the Allison T-63 engine. The performance of these fuels was investigated in the Detroit Diesel 3-53 and 6V-53T engines, Teledyne Continental LDT-465-IC engine, and CUE-1790 engine. The microbiological growth susceptibility of the JP-5 and DFM fuels was investigated at the U.S. Army Natick Laboratories.(2)

^{*} Underscored numbers in parentheses refer to the list of references at the end of this report.

Other evaluations of the Faraho-II fuels performed by the U.S. Air Force, U.S. Navy, Department of Energy, and other government agencies are not the subject of this report but are being accumulated by TRW acting as a data depository under contract with the U.S. Navy (3).

The work conducted at AFLRL is discussed in three sections: FUEL PROPERTIES, GAS TURBINE COMBUSTION PERFORMANCE, and DIESEL ENGINE PERFORMANCE.

II. BACKGROUND

Experiments have determined that the conversion of oil shale into specification fuels is perhaps the most feasible avenue to replace military fuels currently derived from petroleum. In 1975, 10,000 barrels of crude shale oil produced by the Paraho retorting process located at the Naval Oil Shale Reserve, Anvil Points, Colorado, were refined into a product slate of military fuels that included gasoline, JP-4, JP-5/Jet A, DF-2/DFM and heavy fuel oil (4). Because of the lack of adequate hydrotreating facilities at the refinery employed to produce these fuels, the products failed to meet specification requirements primarily in the area of storage and thermal stability. In addition, the DF-2/DFM product was found to contain a high level of particulate and wax at ambient temperatures, which made it unsuitable and caused it to fail existing specifications. However, this work showed that military specification fuels could be produced from oil shale. The fuels produced from this first refined batch of shale have been referred to as Paraho-I fuels.

The fuels derived from a second batch of Paraho shale oil were produced under a joint DOD/DOE project managed by the Navy. In this project, 88,000 barrels of shale oil were produced by the Paraho Development Corporation, sent to the Standard Oil Company (Ohio) refinery in Toledo, Ohio, and processed into finished fuels. A total of 8,000 barrels of gasoline stock or naphtha was produced and retained by SOHIO for further processing. Also, 6,000 barrels of JP-5, 462 barrels of JP-8, 16,000 barrels of marine diesel fuel, and 38,000 barrels of residual fuel oil were produced (1). Fuels generated in this program have been and are here referred to as Paraho-II shale oil fuels.

The processing of this batch of shale oil (1) was described stepwise as follows: Initially, the crude shale oil was allowed to settle at above ambient temperature to reduce water and ash content. After settling, the shale oil was mixed with hydrogen, preheated, and passed through a guard bed where organic iron, arsenic, ash, and solids were removed. Following the pretreatment, the whole shale oil was catalytically hydrotreated at elevated temperatures and under hydrogen partial pressure. In this catalytic reaction of hydrogen with sulfur, oxygen, and nitrogen compounds, the heteroatom content was reduced extensively. Also, aromatic saturation and cracking occurred to some extent, thereby increasing the hydrogen-carbon ratio. The hydrotreated shale oil was fractionated by distillation into gasoline, jet fuel, diesel, and a residual fraction. Some of the residual fraction was recycled to the hydrotreater to increase the jet and diesel fuel yields. Final finishing steps, acid and clay treating, were used on these fuels to meet military specifications for gum and stability.

III. FUEL PROPERTIES

A. Specification Analyses

The properties and characterization of the finished fuels derived from shale oil are shown in Table 1. The properties of the JP-8 are compared to the requirements for Military Specification MIL-T-83133A, Turbine Fuel, Aviation, Kerosene Type, Grade JP-8. An examination of these properties shows that this fuel meets all the requirements for JP-8. The heat of combustion is just above the minimum requirement which correlates with the relatively high aromatic content of this fuel as measured by the FIA procedure. Although this value is within the specification, it is close to the 25 maximum listed in the requirements.

The properties for the JP-5 aircraft turbine fuel are also shown in Table 1 and are compared to the requirements of Military Specification MIL-T-5624L, Turbine Fuel, Aviation, Grade JP-5. The properties of the sample met all the JP-5 requirements except for the smoke point and the copper corrosion test measured at 100°C which gave an ASTM rating of 2c. The maximum rating allowed

TABLE 1. PROPERTIES OF FUELS DERIVED FROM SHALE OIL

		JP-8		JP-5		DFM
Properties	JP-8	Requirements	JP-5	Requirements	DFM	Requirements
Specific Gravity, 15.6/15.6°C	0.8044	0.775-0.840	0.8081	0.788-0.845	0.8353	
Gravity, "API	44.4	37-51	43.6	36-48	37.9	Record
Distillation, °C						
IBP	178		179		206	
10% Recovered	187	205 max	189	205 max	233	
20% Recovered	189 201		192 202		243	***
50% Recovered 90% Recovered	227		202		264 295	357 max
End Point	257	300 max	248	290 max	312	185 max
7 Recovered	98.5		98.5	270 max	99	10.7 11416
2 Residue	1.0	1.5 max	1.5	1.5 max	1	
2 Loss	0.5	1.5 max	0	1.5 max	Ô) max
Flash Point, °C	57	38 min	62	60 min	80	60 min
Viscosity at 37.8°C.eSt	1.30		1.38		2.71	1.8-4.5
Viscosity at -20°C, cSt	4.19	8.0 max	4.68	8.5 max		
Aniline Point, °C	62.4		60.4		67.0	Record
Cloud Point, °C					10	-1 max
Pour Point, °C					-18	-1 max
Freezing Point, °C	-52	-50 max	-51	-46 max		
Existent Gum, mg/100ml	0.4	7 max 0.015 max	0	7 max 0.015 max	0.001	0 1
Total Acid Number, mg KOH/g Neutrality	0.01	0.015 max		0.015 max	Neutral	0.3 max
Aromatics, vol2 (FIA)	21	25 max	22	25 max	30	Neutral
Olefins, volt (FIA)	2	5 max	2	5 max	i	
Carbon, wt%	86.05		85.92		86.54	
Hydrogen, wt%	13.70	13.5 min	13.68	13.5 min	.3.36	
Nitrogen, ppm	0.31		<1		<1	
Oxygen, wt%	0.40		0.38		0.37	
Sulfur, wt%	0.002	0.30 max	0.005	0.40 max	0.004	1.00 max
Thermal Oxidation Stability (JFTOT)						
at 260°C			_			
iP, mm Hg	0	25 max	0	25 max	0	
Tube rating, visual	2	<3	1	<3	3	
TDR-spun TDR-spot	10.0 12.0		2.0 8.0		11.5 19	
Cu Corrosion at 100°C	12.0 1A	18 max	2C	lB max	lA	1 max
Net Heat of Combustion, MJ/kg	42.82	42.8 min	42.68	42.6 min	42.50	1 max
Smoke Point, mm	20.2	19 min	17.5	19 min	16.5	
Aniline-Gravity Product	6.407		6.134	4,500 min		
Visual Appearance	Straw, clear		White, clear		White, clear	Clear, bright
Color, ASTM Rating	0.5		<0.5		<0.5	3 max
Accelerated Stability, mg/100 ml	0.29		0.14		0.20	2.5 max
Particulate Matter, mg/l	0.3	l max	0.1	i max	0.5	8 max
Ash, wt7					0	0.005 max
Cetane Number	45		45		49	45 min
Carbon Residue on					0.01	
10% bottoms, wt% Demulsification, minutes					0.04 5	0.2 max 10 max
Ring Carbon					,	IO max
Mono-aromatics, wt%	13.84		13.54		11.58	
Di-aromatics, wt%	1.19		1.36		4.03	
Tri-aromatics, wt%	9.003		0.002		0.045	
GC Distillation, °C						
0.1 wt% off	120.1		136.5		103.4	
l wt% off	153.6		159.7		152.3	
10 wt% off	170.4	186 max	174.5	185 max	214.0	
20 wt% off	176.6		185.3		236.2	
50 wt% off	203.1		208.9		271.8	
90 wt% off 95 wt% off	241.0		245.9		316.5	
95 Wt% off	252.2 274.6		255.0 278.8		323.3 336.1	
99.5 wt% off	285.7	330 max	291.6	320 max	342.1	
HPLC Aromatics, wt%	23.5		24.9	723 MAX	27.8	
HPLC Saturates, wt%	76.5		75.1		72.2	
· · · · · · · · · · · · · · · · · · ·						

by the specification is lb. The refiners of these shale fuels indicated that they also observed the high copper corrosion rating, and suspected that a small concentration of a sulfur compound remaining in the fuel was causing this rating. It is anticipated that further refining of the shale JP-5 could remove the corrosive material and improve the rating. In future batches of shale oil fuels, this deficiency can be corrected. Again the net heat of combustion is approaching the minimum limit, which is in line with the high aromatic content of this fuel.

The properties of the marine diesel fuel manufactured to meet the requirements of Military Specification MIL-F-16884G, Fuel Oil, Diesel, Marine are also shown in Table 1. The properties are within the specification limits with one exception. The cloud point in the specification is 1°C maximum while the test gave a value of 10°C. The effect of this high cloud point is that engine systems operating in ambient temperatures at or below 10°C may encounter fuel filter plugging due to wax formation. All three of the fuels derived from Paraho-II shale oil were clear in appearance and gave good thermal stability test results. Existent gum and accelerated stability values were low.

Gas chromatographic boiling point distribution analyses were performed on the samples of shale-derived JP-8, JP-5, and DFM and the chromatograms are shown in Figure 1. These indicate that the JP-8 and JP-5 are very similar in composition, with the JP-8 containing more light end components as would be expected due to the lower flash point of JP-8, and that the DFM is composed of higher boiling hydrocarbons. The JP-5 and DFM samples were separated into saturate and aromatic fractions by silica gel chromatography, and the separate fractions were then analyzed by GC boiling point distribution. The chromatograms are shown in Figures 2 and 3 for the JP-5 and DFM fractions, respectively. It appears that in both fuels the light ends are composed more of saturated hydrocarbons and the aromatics are found in the higher boiling portions.

B. Storage Tests at 43°C For 32 Weeks

The three fuels obtained from shale oil were subjected to stability tests at 43° C for 32 weeks($\underline{5}$). After 4, 8, 16, and 32 weeks, pairs of bottles were

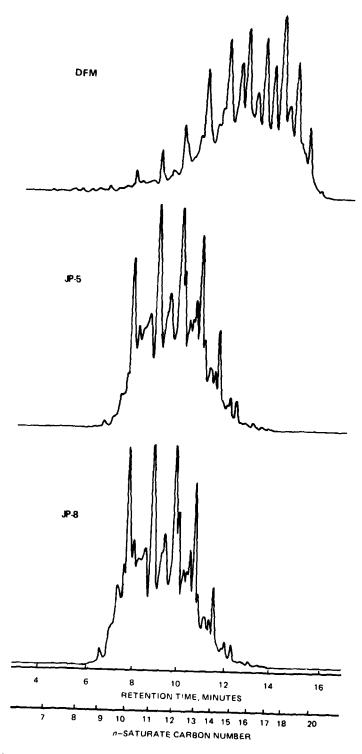


FIGURE 1. GC BPD OF JP-8, JP-5, AND DFM FROM SHALE

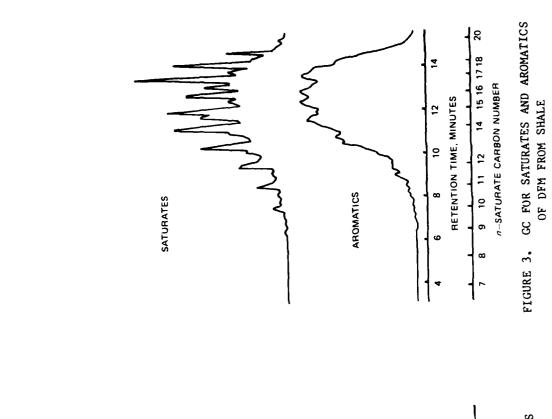


FIGURE 2. GC FOR SATURATES AND AROMATICS
OF JP-5 FROM SHALE

n-SATURATE CARBON NUMBER

SATURATES

AROMATICS

removed from storage and analyzed separately for gum content, dissolved oxygen, and peroxide number. Twelve unvented bottles of each sample were originally placed in storage, and every four weeks, each bottle was cooled overnight and opened for 5 minutes to insure aeration of the samples. As the pairs were removed, they were filtered through sintered-glass filters. filtered fuel was measured for gum content by ASTM D 381. The bottles were rinsed with a triple solvent (equal volumes of toluene, acetone, and methanol) to dissolve adherent gum. The rinses from both bottles were poured through the same sintered-glass filters to dissolve any of the same type of fuel-insoluble, adherent gum that may have remained suspended in the fuel and filtered out during the first filtration. Vaporization of the triple solvent followed, and the insoluble gum was recovered and weighed. Any additional material that remained on the sintered-glass filter was then measured as precipitate by reweighing the filter. Details of this procedure are shown in Appendix A. The results of the storage stability tests are shown in Table 2. The finished fuels manufactured from shale crude oil were stable throughout the 32 weeks of storage at 43°C and compared favorably with a petroleum-based JP-5 subjected to the same test. Only small amounts of gum were formed in each sample. The soluble and the insoluble gum and precipitate levels formed during each storage period for each of the fuels are plotted in Figures 4 through 6.

It is generally acknowledged that autoxidation in hydrocarbon liquids is a chain reaction involving peroxy and hydrocarbon free radical(6). There is a period in this process during which little oxygen is absorbed and only small amounts of oxidation products are formed. After this induction period, peroxides are formed, followed by insoluble oxidation products. Dissolved oxygen content and peroxide numbers of stored samples were measured after 4, 8, 16, and 32 weeks in an attempt to identify the induction period. The data are shown in Table 3. The shale fuels initially had a dissolved oxygen content which remained at approximately the same level through 16 weeks of storage. At 32 weeks, the dissolved oxygen levels were reduced significantly, a fact which suggests the induction period ended sometime between 16 and 32 weeks. The finished fuels from shale oil showed no measurable peroxide number until 8 weeks of storage and slight increase in values after 16 and 32 weeks. The 16-week samples for the JP-8 fuel were lost before peroxide numbers were measured.

TABLE 2. STORAGE STABILITY TESTS AT 43°C mg/100 ml

				4 Weeks			8 Weeks	
Code No.	Description	Initial	Soluble	Insoluble gum	Precipitate	Soluble	Insoluble	Precipitate
AL-8466-T	JP-8 from Paraho-II Shale Oil	0.4	A-i.2* B-1.2*	0.7	0.1	A-0.9 B-0.9	9.0	0.1
AL-8436-T	JP-5 from Paraho-II Shale Oil	0	A-0 B-0	6.5	0.1	A-0 B-0	7. 0	0.1
AL-8437-T	DFM from Paraho-II Shale Ofl	0	A-0 B-0	9*0	9*0	A-0.6 B-0.5	6•0	1.0
AL-6400-T	AL-6400-T Petroleum-Based JP-5	0.3	9•0	1.4	0.1	1.7	0.5	0
				16 Weeks	S		32 Weeks	
Code No.	Description		Soluble	Insoluble gum	Precipitate	Soluble gum	Insoluble gum	Precipitate
AL-8466-T	JP-8 from Paraho-II Shale Oil		A-1.1 B-1.0	1.0	0.2	A-1.7 B-1.7	2.3	0.3
AL-8436-T	JP-5 from Paraho-II Shale Ofl		A-0 B-0	0.7	9*0	A-0 B-0	0.8	0.2
AL-8437-T	DFM from Paraho-II Shale Oil		A-0 B-0	6*0	1.0	A-0.5 B-1.2	1.4	1.0
AL-6400-T	Petroleum-Based JP-5		0.5	0.7	0.02	2.6	1.7	6*0

* A and B are values obtained for duplicate bottles. The insoluble gum and precipitate values for bottles A and B are combined into one.

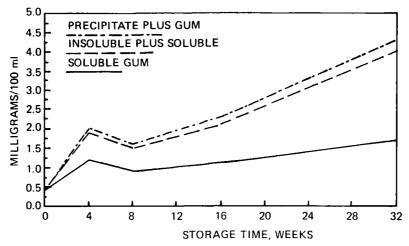


FIGURE 4. STORAGE STABILITY TEST AT 43°C FOR JP-8 FROM SHALE OIL

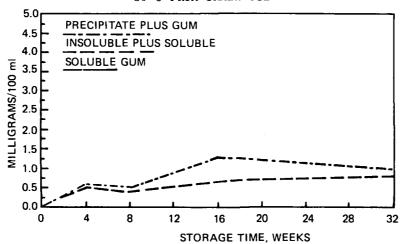


FIGURE 5. STORAGE STABILITY TEST AT 43°C FOR JP-5 FROM SHALE OIL

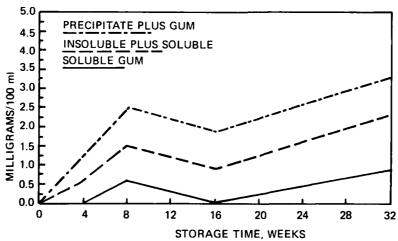


FIGURE 6. STORAGE STABILITY TEST AT 43°C FOR DFM FROM SHALE OIL

TABLE 3. DISSOLVED OXYGEN AND PEROXIDE NUMBERS IN FUELS STORED AT 43°C

		Ini	Initial	4 Weeks	eks	8 Weeks	eks
Code No.	Description	Dissolved O ₂ , ppm	Dissolved Peroxide 02, ppm Number*	Dissolved Peroxide	Peroxide Number*	Dissolved Peroxide	Peroxide Number*
AL-8466-T	JP-8 from Paraho-II Shale Oil	69	0	67	0	67	0.14
AL-8436-T	JP-5 from Paraho-II Shale Oil	72	0	69	0	09	90°0
AL-8437-T	DFM from Paraho-II Shale Oil	54	0	52	0	52	0.33
Code No.	Description	16 V Dissolved	16 Weeks Dissolved Peroxide O2, ppm Number*	32 We Dissolved O2, ppm	32 Weeks ved Peroxide pm Number*		
AL-8466-T	JP-8 from Paraho-II Shale Oil	*	*	45	0.24		
AL-8436-T	JP-5 from Paraho-II Shale Oil	85	0.12	42	0.16		
AL-8437-T	DFM from Paraho-II Shale Oil	46	0,35	34	0.39		

* Peroxide number is defined as the gram-equivalent of active oxygen in 1000 liters of fuel. ** Sample lost.

The shale oil-derived fuels were stable with respect to the 32-week, 43°C storage test and did not generate sufficient quantities of gum for analyses. Thermal oxidation stability tests by the JFTOT procedure were conducted on the shale fuels, and the data shown in Table 4 indicate those fuels to be thermally stable. The jet fuels, JP-8 and JP-5, met the specification require-

TABLE 4. THERMAL OXIDATION STABILITY (JFTOT) DATA FOR SHALE-DERIVED FUELS BEFORE AND AFTER 32 WEEKS OF STORAGE AT 43°C

JFTOT at 260°C	JP-8	<u>JP-5</u>	DFM
As Received			
Δ P, mm Hg	0	0	0
Tube rating, visual	2	1	3
Tube Deposit Rating, spun	10.0	2.0	11.5
Tube Deposit Rating, spot	12.0	8.0	14.0
After 32 weeks at 43°C			
Δ P, mm Hg	0	0	0
Tube rating, visual	2	1	1
Tube Deposit Rating, spun	2	4	7
Tube Deposit Rating, spot	7.5	6	14

ments. The DFM had a visual tube rating of 3, which would be a fail for jet fuels; however, after storage, the DFM had a visual tube rating of 1, suggesting that most of the unstable species had been removed as gum.

C. Hydrocarbon Type Composition of Fuels

The hydrocarbon type composition of the fuels from coal and from shale was determined by several techniques: fluorescent indicator adsorption (FIA), proton nuclear magnetic resonance (proton NMR), natural abundance carbon-13 nuclear magnetic resonance (13 C NMR), and aromatic carbon by ultraviolet spectrometry. The FIA is a standard ASTM procedure used for petroleum-derived gasolines and jet fuels but is not reliable when used with diesel fuels. The proton NMR technique was described by Myers, et al.(7) and can be used to calculate aromatics, olefins, and saturates in the sample as well as hydrogen-carbon ratio. The calculations are based on equations derived from properties of hydrocarbons in the gasoline range; therefore, this technique may not be entirely applicable to hydrocarbons of higher molecular weights present in the samples in this investigation. The 13 C NMR method described by Shool-

ery and $\operatorname{Budde}(8)$ measures the aromatic carbon atoms present in the sample, and the balance is assumed to be paraffinic carbons. The ultraviolet technique distinguished between the single-ring, the double-ring, and the triple-ring aromatic carbon atoms.

Table 5 contains the hydrocarbon type data for fuel samples before and after the storage tests. The shale-derived fuels were analyzed by FIA, proton NMR,

FIA (as received) Aromatic, vol% Olefin, vol% Proton NMR (as received) Aromatic, vol% Olefin, vol% Proton NMR (32 weeks) Aromatic, vol% Olefin, vol% C NMR (as received) Aromatic, w+% 15.4 13.1 13.1 13.1 14.3 15.4 15.4 16.4 17.1 18.1 19.1	
Aromatic, vol% 21 22 3 Olefin, vol% 2 2 2 Proton NMR (as received) Aromatic, vol% 16 14 14 16 16 16 17 17 18 17 18 18 18 19 18 18 18 18 18 18 18 18 18 18 18 18 18	DFM
Olefin, vol% 2 2 Proton NMR (as received) Aromatic, vol% 16 14 14 16 16 16 17 17 18 17 18 18 18 18 18 18 18 18 18 18 18 18 18	
Proton NMR (as received) Aromatic, vol% 16 14 16 16 16 17 17 18 18 18 18 18 18 18 18 18 18 18 18 18	30
Aromatic, vol% 16 14 16 16 16 16 16 17 17 18 18 18 18 18 18 18 18 18 18 18 18 18	1
Olefin, vol% 5 0 Proton NMR (32 weeks) Aromatic, vol% 15 13 13 10 15 13 15 15 15 15 15 15 15 15 15 15 15 15 15	
Proton NMR (32 weeks) Aromatic, vol% 15 13 13 10 15 13 15 15 15 15 15 15 15 15 15 15 15 15 15	1.5
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Olefin, vol% 5 2 13 C NMR (as received) Aromatic, w*% 15.4 14.3 1 13 C NMR (32 weeks) Aromatic, wt% 15.0 15.6 1 Ultraviolet (as received)	
13 C NMR (as received) Aromatic, w*% 15.4 14.3 1 13 C NMR (32 weeks) Aromatic, wt% 15.0 15.6 1 Ultraviolet (as received)	16
Aromatic, w*% 15.4 14.3 1 13 C NMR (32 weeks) Aromatic, wt% 15.0 15.6 1 Ultraviolet (as received)	4
Aromatic, w*% 15.4 14.3 1 13 C NMR (32 weeks) Aromatic, wt% 15.0 15.6 1 Ultraviolet (as received)	
13 C NMR (32 weeks) Aromatic, wt% 15.0 15.6 1 Ultraviolet (as received)	5.0
Aromatic, wt% 15.0 15.6 1 Ultraviolet (as received)	-
Aromatic, wt% 15.0 15.6 1 Ultraviolet (as received)	
	3.2
III OHINE TO GOLOGIA	
Mono, wt% 13.84 13.54 1	1.58
Di, wt% 1.19 1.36	4.03
Tri, wt% 0.002 0.002 0	.045

 $^{^{13}}$ C NMR, and UV before the storage test. The two NMR techniques also were used to analyze the samples after the 32-week, 43°C, storage test. In view of the differences in the methods as described above, it is not surprising that the values shown in Table 5 differ among the methods. When comparing the values obtained by NMR on the original samples to those after 32 weeks, very few differences were observed for the shale fuels. Both proton NMR and 13 C NMR spectra for fuels before and after storage are shown in Appendices B and C, respectively.

D. Compatibility With Petroleum Fuels

The compatibility of shale-derived fuels with petroleum fuels under conditions designed to accelerate the oxidation process was investigated. Blends of equal quantities of the shale JP-5 with petroleum-derived JP-5, and the shale DFM with petroleum-derived diesel fuel were subjected to stability tests at 150°C and 80°C.

The High Temperature Stability of Distillate Fuels is a procedure being considered by ASTM for standardization and is summarized as follows: A measured volume of distillate fuel is aged 1.5 hours at 150°C in an open tube with air exposure. After aging and cooling, fuel is filtered and the amount of insoluble residue formed is estimated by determining the light reflectance of the filter pad. In this work, the procedure was modified to include a gravimetric determination of the residue, measurement of light absorbance of the fuel at four wavelengths, and steam jet gum on the fuel after aging and filtering. In addition, the adherent gum remaining in the sample aging bottles was measured.

The data for the JP-5 evaluations are shown in Table 6 and indicate that no compatibility problems were observed with these two fuels when filterable particulates formed at 150°C are the criteria for consideration. The levels of particulates formed in the blended fuel are about midway between the level formed in the shale JP-5 and in the petroleum JP-5. Fewer particulates were formed in the shale JP-5 than in the petroleum JP-5. The steam jet gum measured on the filtered fuels have slightly higher gum levels in the blend than in either the shale or petroleum JP-5.

Evaluations of shale DFM, petroleum DF-2 and 50/50 blends in the 150°C modified stability test are presented in Table 7. As in the case of JP-5 fuels, the level of particulates formed in the blended fuel samples was somewhere between the level formed in each fuel. The shale-derived DFM produced less particulates than the petroleum DF-2. Steam jet gum measurements on the filtered blended fuel samples were considerably higher than those for the individual fuels. The higher steam jet gum values for the blends of JP-5 and diesel fuels may indicate some synergism between shale oil and petroleum products during oxidation reactions under these aging conditions.

TABLE 6. COMPATIBILITY OF SHALE AND PETROLEUM JP-5 FUELS Modified $150^{\rm o}{\rm C}$ Test

	_					
Code No.	AL-84	36-T	AL-8	570-T	AL-8436-T	& AL-8570-T
Fuel Description	Paraho-	II JP-5	Petrole	um JP-5	Blend	50/50
Test hr	1.5	3.0	1.5	3.0	1.5	3.0
Color after test,						
D 1500 (1)	0.5	0.5	0.5	0.5	0.5	0.5
Glass Fiber Filter						
Rating, Visual (2)	1	5	15	19	12	15
% Reflectance (3)	93.9	86.0	50.8	32.0	68.8	55.0
Wt of particulates,						
mg/100 ml	0.08	0.12	0.56	1.04	0.26	0.48
Light Absorbance,						
650 nm	0	0	0	0	0	0
575 nm	0	0.002	0	0.004	0	0
540 nm	0.001	0.007	0.006	0.015	0.001	0.005
500 nm	0.002	0.019	0.015	0.035	0.005	0.012
Adherent Insolubles,						
mg/100 m1	0.2	0.2	0.1	0.2	0.2	0.3
Steam Jet Gum on						
filtered sample,						
mg/100 ml	0.4	1.6	1.6	3.2	3.6	4.8

⁽¹⁾ Color of original samples and blends: 0.5

TABLE 7. COMPATIBILITY OF SHALE AND PETROLEUM DIESEL FUELS Modified 150°C Test

Code No. Fuel Description Test hr	AL-84 Paraho- 1.5	_	AL-82 Petroleum	DF-2	AL-8437-F & AL- Blend 50/50	
Color D 1500				- <u></u>		
before test	0.5	0.5	1.5	1.5	1.0	1.5
after test	0.5	0.5	1.5	1.5	1.0	1.5
Glass Fiber Filter						
Rating, Visual (1)	1	2	17	20	8	20
% Reflectance						
Filter	95.8	94.1	40.5	18.5	79.0	27.5
Control	99.0	97.8	95.0	96.0	95.0	95.1
Wt of particulates,						
mg/100 ml	0.06	0.16	0.59	0.90	0.24	0.59
Light Absorbance,						
650 nm	0	0.001	0.004	0.008	0	0.004
575 nm	0	0.008	0.023	0.031	0.011	0.019
540 nm	0	0.016	0.043	0.057	0.019	0.034
500 nm	0	0.035	0.088	0.114	0.040	0.067
Adherent Insolubles,						
mg/100 ml	0.2	0.2	0.2	0.2	0.1	0.2
Steam Jet Gum on						
filtered sample,						
mg/100 ml	1.2	3.8	4.0	4.2	16.0	13.6

⁽¹⁾ Visual rating for all control filters: 1

⁽²⁾ Visual rating for all control filters: 1

^{(3) %} Reflectance for all control filters: 99.0%

The 80°C Accelerated Fuel Oil Stability Test is a method developed by an additive manufacturer's petroleum laboratory to determine the stability of distillate fuels such as home heating oils or diesel oils under accelerated conditions within 7 to 14 days. The sample is aged at 80°C for up to 14 days, cooled and vacuum filtered through a filter paper to collect residues. The filter pad is compared to a set of standards to obtain a numerical visual rating or is rated by a reflectance rating. At AFLRL the method was modified so that residues were weighed and the fuel samples were examined for light absorbance in a UV-visible spectrophotometer at 650, 575, 540, and 500 nm. In addition, the samples were analyzed for adherent gum in the aging containers and existent gum content by the steam jet procedure.

Data for the stability tests of the shale JP-5, petroleum JP-5, and a 50/50 blend of these two fuels at 80°C for 3, 7, and 14 days are shown in Table 8. Under these conditions, the stability of shale JP-5 was poor when compared to the data for petroleum JP-5. The blend of the two fuels gave results comparable to or even better than those for the petroleum JP-5. Repeat tests for 7 and 14 days of the Paraho-II JP-5 were conducted and gave about the same results as the original tests. The stability test results at 80°C for the shale DFM, the petroleum DF-2, and a blend of these two fuels, for 3, 7, and 14 days, are shown in Table 9. As in the case of JP-5 fuels, the shale DFM gave poorer results than the petroleum-based DF-2, and the blend gave comparable or slightly better results than the petroleum DF-2. Repeat tests on the shale DFM for 7 and 14 days gave about the same results as the first tests. There appears to be no compatibility problem under these conditions between the shale and petroleum fuels; however, it is apparent that relatively more rapid oxidation of the shale-derived fuels takes place at 80°C than at 150°C or at 43°C.

E. Additive Response

The response of additives designed for petroleum fuels in the shale-derived fuels was investigated in two areas: cetane number improvement and corrosion inhibition. Paraho-II JP-8, JP-5, and DFM were treated with 0.1, 0.25, and 0.5 vol% of 2-ethyl hexyl nitrate*, and each blend as well as the neat fuels

^{*} Ethyl Corporation's DII-3.

COMPATIBILITY OF SHALE AND PETROLEUM JP-5 FUELS--MODIFIED 80°C OXIDATION TEST TABLE 8.

Code No.		AL-8436-T			AL-8570-T		AL-84	AL-8436-T and AL-8570-T	570-T
Fuel Description	Pa	Paraho II JP-5		Petro	Petroleum-Based	JP-5		50/50 Rlend	
Test Days			14	3	1	14			14
Color, D 1500, Before/After	0.5/0.5	0.5/0.5	0.5/3.5	0.5/0.5	0.5/0.5	0.5/0.5	0.5/0.5	0.5/0.5	0.5/0.5
Repeat test	1	0.5/0.5	0.5/3.0	1	;	:			
Glass Fiber Filter Rating									
Visual - Top/Control	2/1	1/1	20/1	6/2	11/3	13/2	2/1	6/1	4/1
Repeat test	;	20/4	19/1	;	;	;	. ;	. ;	.
% Reflectance - Top/Control	91.2/98.5	79.5/100	0,88,0	83.9/93.0	70.9/87.0	52.2/90.9	92.9/98.1	81.9/98.3	90.9/98.3
Repeat test	!	53.5/97	2/90	;	;	•			•
Weight of Particulates, mg/100ml	0.10	0.47	22.16	0.08	0.22	0.36	90.0	0.10	0.22
Repeat test	-	0.88	21.82	;	;	;	;	;	;
Light Absorbance,									
650 nm	0	0	0.030	0	0.001	0	0	0	0
Repeat	!	0	0.025	;	;	;	;	:	;
575 nm	0	0.001	0.119	0.002	0,005	0.005	0	0	0
Repeat		900.0	0.098	;	;	;	;	;	;
540 nm	0	0.099	0.235	0.008	0.013	0.015	0	0.002	0.003
Repeat	;	0.017	0.193	***	1	;	;	;	!
\$00 nm	0	0.027	0.497	0.015	0.024	0.030	0.003	900.0	0.008
Repeat	-	0.042	0.414	;	:	;	;	;	;
Adherent Insolubles, mg/100mi	0.3	0.85	60.5	0.05	0.75	1,45	0.20	0.10	0.65
Repeat test	1	2,20	4.85		::	;	;	;	1
Steam Jet Sum on									
Filtered Sample, mg/100ml	0.2	24.2	31.3	7.9	1.2	1.0	0.8	0	9.0
Repeat test	;	13.2	56.4	;	;	;	;	!	-

TABLE 9. COMPATIBILITY OF SHALE AND PETROLEUM DIESEL FUELS--MODIFIED 80°C OXIDATION TEST

Code No.		AL-8437-F			AL-8277-F		AL-84	AL-8437-F and AL-8477-F	477-F
Fuel Description Test Days	~	Paraho II DFM	14	Petro	leum-Based	DF-2	-	50/50 Blend	7,
				,					
Color, D 1500, Before/After	0.5/0.5	0.5/1.5	0.5/3.5	1.0/1.0	1.0/1.0	1.0/1.5	0.5/0.5	0.5/0.5	0.5/0.5
Repeat test	;	0.5/1.0	0.5/3.0	:	;	;	;	;	-
Glass Fiber Filter Rating									
Visual - Top/Control	3/1	14/2	20/2	8/2	10/2	10/2	3/2	3/2	3/2
Repeat test	i	17/2	20/2	;	;	;	i	;	;
2 Reflectance - Top/Control	92.5/100	0.96/0.99	0/99.5	77.5/94.0	73.5/93.2	68.9/93.2	92.0/97.1	90.5/96.0	87.2/95.6
Repeat test	!	44.5/97.5	2.5/92.0	;	;	;	;	1	}
Weight of Particulates, mg/100ml	0.02	2.02	43.26	0.02	0.18	0.18	0.14	0.14	0.04
Repeat test	1	2.06	25,58	;	;	;	i	1	-
Light Absorbance,									
650 nm	0	0.001	0.028	0.003	0.005	9000	0	0	0
Repeat	•	0.002	0.034	* * * * * * * * * * * * * * * * * * * *	;	;	;	;	;
575 ram	0	0.015	0,123	0.018	0.020	0.025	0.007	0.007	0.008
Repeat	ļ	0.013	0.111	;	!	;	į	;	;
540 nm	0	0.038	0.260	0.036	0.040	0.049	0.015	0.017	0.020
Repeat		0.030	0.209	!	-		;	;	
500 nm	0	0.099	0.604	0.075	0.084	0.101	0.035	0.037	0.044
Repeat	ļ	0.078	0.472	!	;	;	;	;	;
Adherent Insolubles, mg/100m1	0.2	0.5	6.9	0.3	0.2	0.3	0.2	0.2	0.3
Repeat test	!	0,3	2.4	i	;	;	i	;	1
Steam Jet Gum on									
Filtered Sample, mg/100ml	9.0	42.8	88.2	23.8	5.2	4.2	20.6	2.6	0.2
Repeat test	1	29.6	153.2	!	;	;	;	;	į

were evaluated for cetane numbers. The data are presented in Table 10 and plotted in Figure 7. The curve in Figure 7 for the petroleum fuel is based on data supplied by the additive manufacturer. The Paraho-II shale fuels appear to be responsive to cetane improver additives in approximately the same manner as a petroleum fuel.

	TABLE 10.	EFFECTS	OF CETANE IMPR	OVER ADDITIVES	
Sample_		Neat	0.1 vo1% DII-3	0.25 vol% 	0.5 vol% DII-3
JP-8, AL-9089-SP		45	50	55	59
JP-5, AL-8436-T		44	50	53	56
DFM, AL-8437-F		49	55	59	64

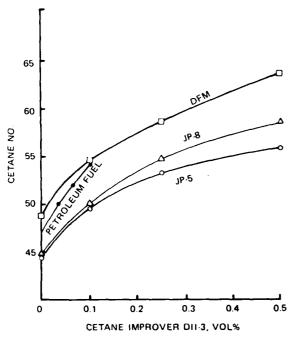


FIGURE 7. EFFECT OF CETANE IMPROVER (DII-3) ON CETANE NUMBERS OF SHALE-DERIVED FUELS

Corrosion tests determined on the shale fuels resulted in "C" ratings for the JP-8 and JP-5 fuels and a "B" rating for the DFM as shown in Table Addition of 25 pounds per thousand barrels of FOA-15 (an additive package containing dispersant, oxidation and corrosion inhibitors, and a metal deactivator) improved the ratings for JP-5 and DFM but not for the JP-8. This additive package is the candidate stabilizer additive for diesel fuel, Purchase Description PD These tests indicate that ME-103. these fuels appear to have corrosion tendencies and are not completely inhibited by the additive package FOA-15 at the concentration used.

TABLE 11. CORROSION TENDENCIES OF SHALE FUELS

	NACI	E Corrosion Ratings
	Neat	25 PTB** FOA 15***
JP-8, AL-9089-SP	С	С
JP-5, AL-8436-T	С	B+
DFM, AL-8437-F	В	B++

^{*} NACE - National Association of Corrosion Engineers.

Rating Descriptions:

A - no rusting	B - 5 to 25% rusting
B++ - less than 0.1% - 2 spots of no	C - 25 to 50% rusting
more than 1 mm in diameter	D - 50 to 75% rusting
<u>B+ - less th</u> an 5% rusting	E - 75 to 100% rusting
B+, B++, and A are acceptable ratings fo	r pipeline operation.

F. Microbiological Growth Susceptibility

Samples of the shale-derived JP-5 and DFM were submitted to the U.S. Army Natick Laboratories for investigations of the microbiological growth susceptibility of these materials(2). As reported by the Natick Laboratories, the samples were tested in duplicate by placing 10 ml of Bushnell Haas medium in 150 x 20 mm screw cap test tubes and overlayed with 3 ml of the test fuel. Each tube was inoculated with one drop of a spore suspension of Cladosporium resinae, QM 7998, grown on potato dextrose agar, and incubated at 30°C. Table 12 shows the results of microbial susceptibility to the test fuels.

TABLE 12. GROWTH RATING OF CLADOSPORIUM RESINAE IN TUBES AFTER DAYS OF INCUBATION

		Length of	Time	
Fuel 30	days 60 days	90 days	120 days	6 Months
Shale JP-5	+* •	ů.	•	•
Shale DFM	•	•	•	•

* Rating

- + = good growth
- = heavy growth

^{**} PTB - pounds per thousand barrels.

^{***} FOA 15 - Fuel oil additive 15 - candidate stabilizer additive for diesel fuel, Purchase Description PD ME-103.

Heavy growth of the <u>Cladosporium resinae</u> in the Shale JP-5 and DFM samples was noted between the second and third months of incubation, concentrated at the interface between the fuel and the Bushnell Haas solution. The growth of <u>Cladosporium resinae</u> observed on the shale JP-5 and DFM confirms earlier observations by May and Neihof(9) who found Paraho-II JP-5 supported good growth. However, reports of growth on shale-derived DFM have not been found in the literature.

IV. GAS TURBINE COMBUSTION PERFORMANCE

For gas turbine combustion, the fuel properties of greatest concern are the chemical composition, the distillation curve, and the viscosity. The first property is generally associated with flame radiation and exhaust smoke; the latter two affect atomization and vaporization, and therefore, ignition, gaseous emissions, combustion efficiency, and flame stability. Fuel-bound nitrogen is one new fuel property that has emerged from the use of syncrude fuels, primarily shale oil, because of the additional NO found in the exhaust. Synthetic fuels have been suspected of having a greater propensity to form soot because of the higher concentrations of polycyclic compounds, namely aromatics, which have been shown in some instances to form more soot than similar fuels containing monocyclic aromatics.

In this work, the combustion performances of shale-derived JP-5 and DFM fuels have been compared with that of a typical petroleum fuel such as Jet A. Combustion performance included the measurement of flame radiation, exhaust smoke, gaseous emissions (CO, exhaust hydrocarbons, NO_{χ}), and combustion efficiency.

A. Experimental Program

The experiments were conducted in the gas turbine combustor laboratory at the U.S. Army Fuels and Lubricants Research Laboratory. This facility was designed specifically for fuels research in gas turbine engines. Basically, the air factory can deliver unvitiated, pulsation-free air at a rate of 1.1 kg/sec at pressures up to 15 atm and temperatures as high as 827°C. The fuel pump is the gear type from an Allison T-63 engine driven by an SCR-controlled DC motor.

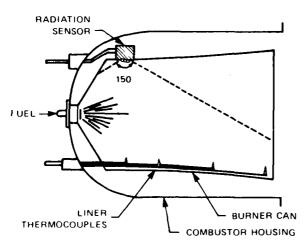


FIGURE 8. FLAME RADIATION MEASUREMENT

The combustor rig is based on hardware from the Allison T-63 engine. The burner is a single-can type with a dual orifice, pressure atomizer centered in the dome as shown in Figure 8. Ignition is by a surface-gap, repetitive-spark igniter located adjacent to the atomizer.

Radiation from the primary zone is measured by a water-cooled bolometer-type radiation sensor attached to the side of the burner. The sensor has a sapphire window and a viewing angle of 150 degrees. At the exit of the burner can there is a centerbody

that diverts the flow into an annulus where nozzles and turbine blades are normally located. Gas sampling probes, pressure sensors, and thermocouples are arranged circumferentially in one plane of the annulus at various radial positions.

Table 13 presents the operating conditions which represent the air flow rates in the actual engine for the six different power points (idle to full power) investigated.

B. Data Acquisition System

The heart of the data acquisition system is a programmable calculator which is coupled to a scanner and digital voltmeter to automatically acquire data and process it. Operating conditions are then printed out for monitoring on a thermal line printer with an update about every ten seconds. The flow rates of the combustor air and fuel are measured with turbine flowmeters. All pressures are sensed with strain-gauge transducers activated by regulated power supplies. Chromel alumel thermocouples, referenced to a 66°C regulated oven, are used for temperature measurement. A summary report of the test conditions

TABLE 13. T-63 COMBUSTOR RIG OPERATING CONDITIONS

Mode	Percent Power	BIP, kpa	BIT, °K	ω_a , kg/s	ω_{f} , kg/m	F/A
Ground Idle	10	230	422	0.64	0.42	0.0109
	25	283	452	0.75	0.54	0.0121
Descent	40	329	478	0.86	0.68	0.0131
Cruise	55	369	294	0.93	0.93	0.0145
Climb/Hover	75	418	518	1.02	1.01	0.0166
Takeof f	100	477	547	1.10	1.30	0.0198

BIP: Burner inlet air pressure

BIT: Burner inlet air temperature

exhaust emissions, and combustion efficiency.

 $\begin{array}{ccc} \omega & \text{:} & \text{Air flow rate} \\ \omega & \text{f} & \text{Fuel flow rate} \end{array}$

Fuel/air ratio

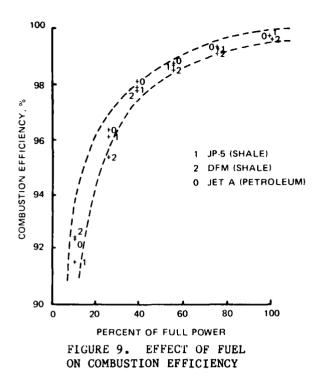
is printed at the end of each run which includes averages and standard deviations of the air and fuel flow parameters, exhaust temperature profiles,

Exhaust Gas Analysis

Exhaust emissions were measured on-line with a non-dispersive infrared analyzer for CO and CO₂, a flame ionization detector hydrocarbon analyzer, a chemiluminescence analyzer for $\mathrm{NO}_{_{\mathrm{X}}}$, and a field oxygen analyzer. The SAE ARP-1179 method was used for measuring exhaust smoke. The correlation of Troth et al. was used to convert smoke number to particulate concentration(10). Combustion efficiencies were calculated from the exhaust gas analysis according to a relationship developed by Hardin(11).

Results and Discussions

A tabulation of the combustion performance data for shale-derived JP-5 (fuel 1) and DFM (fuel 2) compared to a petroleum Jet A (fuel 0) is given in Table 14. In general, the combustion properties of synthetic JP-5 and DFM are not significantly different from the respective petroleum-derived fuels. Figures 9 through 12 show the effect of operating conditions on combustion efficiency and gaseous emissions (CO, total exhaust hydrocarbons, and NO_{v}). Combustion efficiency increases as power is increased; significant differences due to fuel property effects are observed only at the lower power points where fuel



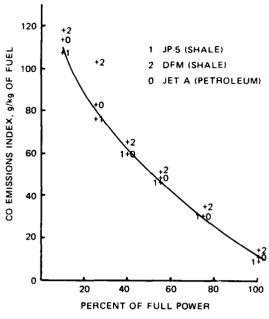
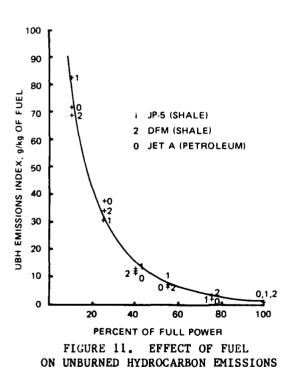


FIGURE 10. EFFECT OF FUEL ON CARBON MONOXIDE EMISSIONS



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vaporization and mixing are poor. Jet A and JP-5 have similar viscosities and boiling point distributions, so it is expected that they would have about the same combustion efficiencies. DFM is expected to burn less efficiently because it is a higher boiling point fraction with a greater viscosity.

			TABLE 1	4. SUM	MARY OF	EXPERIME	NTAL RESU	ILTS	····
Power	Fuel	Fuel	Flame	Smoke	Smoke	NO *	CO	ИВН	Combustion
Point	No.	Type	Radia.	No.	mg/M^3	E.I.	E.I.	E.I.	Efficiency
100	0	Jet A	42.8	28.9	4.3	7.2	9.5	0.2	99.79
100	1	JP-5	59.7	48.7	13.2	7.2	9.1	0.4	99.78
100	2	DFM	60.1	45.2	10.8	6.7	13.8	0.4	99.67
75	0	Jet A	37.0	32.1	5.1	5.5	30.3	2.0	99.31
75	1	JP-5	48.9	38.1	7.1	5.7	30.8	1.9	99.28
75	2	DFM	50.7	41.0	8.46	4.7	34.3	2.9	99.13
5 5	0	Jet A	31.9	15.8	1.8	4.7	48.3	7.1	98.64
55	1	JP-5	43.7	19.7	2.4	4.6	47.7	7.3	98.59
55	2	DFM	48.1	22.6	2.9	4.3	50.1	7.0	98.54
40	υ	Jet A	26.7	12.0	1.3	4.7	59.6	11.7	98.14
40	l	JP-5	37.4	25.2	3.4	4.7	59.9	13.3	97.97
40	2	DFM	43.2	27.9	4.0	4.7	65.4	12.5	97.91
25	0	Jet A	23.3	11.7	1.27	3.1	82.3	35.9	95.57
25	1	JP-5	30.0	21.2	2.6	3.6	75.8	30.7	96.13
25	2	DFM	39.2	29.9	4.5	3.3	102.3	33.7	95.35
10	0	Jet A	17.8	7.9	0.84	1.3	113.6	71.5	92.37
10	1	JP-5	26.2	17.7	2.06	3.3	107.9	82.9	91.52
10	2	DFM	31.9	23.2	3.0	3.1	118.0	69.0	92.42

Combustion inefficiency is determined by the amounts of carbon monoxide and unburned hydrocarbons in the exhaust. Figure 10 shows that the DFM gives slightly higher CO emissions than the Jet A and JP-5. Interestingly, the unburned hydrocarbon emissions shown in Figure 11 are about the same for both test fuels and Jet A. In fact, the DFM gives somewhat lower emissions, which is contrary to its higher viscosity and boiling point fractions. This appears to be caused by the nature of the combustion process in the T-63 burner. The rate of burning appears to be limited more by the mixing of fuel with air than by fuel vaporization.

The NO_{X} emissions shown in Figure 12 were essentially the same for both shale fuels and Jet A at all the operating conditions. If the shale fuels had contained fuel-bound nitrogen, there would have been an increase in the NO_{X}

emissions index. Thermal NO_X , formed by the oxidation of nitrogen (Zeldovich reaction), depends on the peak flame temperature and the residence time of hot gases in the combustor. Fuel properties, such as heat of combustion and heat of vaporization which affect flame temperature, would change the rate of NO_X formation.

Soot formation in gas turbine engines is detected as exhaust smoke and increased combustion chamber liner temperature, i.e., radiant heat transfer from incandescent carbon particles. The flame radiation intensity increases as the flame temperature and the soot concentration increase. Exhaust smoke is what remains after about 98 percent of the soot is oxidized in the secondary and quench zones of the combustor ($\underline{12}$); these oxidation rates are dependent on combustor operating conditions, such as burner inlet air temperature, and do not appear to be affected by fuel properties.

Several studies (13 through 17) have shown that soot formation correlates strongly with the H/C ratio or hydrogen content of the fuel. The H/C ratio has been found to be a good correlating parameter for synthetic fuels, water/fuel emulsions, alcohol/fuel blends, and microemulsions. Figures 13 and 14

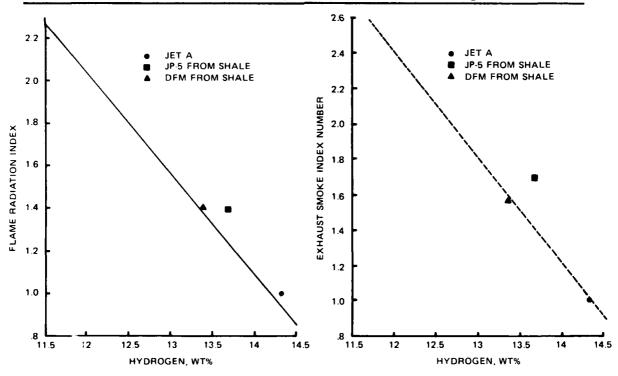


FIGURE 13. CORRELATION OF FLAME RADIATION WITH HYDROGEN CONTENT

FIGURE 14. CORRELATION OF EXHAUST SMOKE WITH HYDROGEN CONTENT

show correlations of hydrogen content with flame radiation and exhaust smoke. The correlations only include data for the full power operating condition. At this condition, the tendency to form soot is the greatest and the combustion efficiency is very high (>99.5%). The actual curves are based on earlier data obtained from petroleum-derived fuels. The radiation and smoke indices are relative values which correspond to the quotient of the observed and reference (Jet A) values. The flame radiation and exhaust smoke indices for the JP-5 shale oil-derived fuel deviate somewhat from the petroleum fuel correlations, but the DFM fuel is in good agreement. It has been found in earlier studies that synthetic fuels from tar sands, shale oil, and coal correlate with hydrogen content in the same way as petroleum-based fuels(15,16).

V. DIESEL ENGINE PERFORMANCE

Engine tests were conducted to determine if the maximum power output and specific fuel consumption obtained with the shale-derived JP-5 and DFM were comparable to that obtainable with similar petroleum-derived products. The method of analysis chosen was to compare the engine results obtained with these fuels to those of a reference petroleum diesel fuel. Any differences in performance which could not be explained by differences in fuel properties would indicate possible influences resulting from the shale fuel source.

Three diesel engines were used during maximum power output and specific fuel consumption testing; the militarized version of the Detroit Diesel 6V-53T, the military developed LDT-465-1C, and a single cylinder from the Teledyne-Continental AVDS-1790 air-cooled diesel mounted on a CUE crankcase. A commercially configured Detroit Diesel 3-53 diesel engine was operated for 210 hours with the shale-derived DFM according to the Army/CRC wheeled-vehicle endurance cycle to evaluate the wear and deposit formation tendencies of this fuel.

The engines used in these evaluations represent critical and widespread engines in the military tactical fleet. Their characteristics are shown in Table 15. The LDT-465-1C multifuel engine is one model of the highest density engine design in the military fleet. The Detroit Diesel 6V-53T engine is considered to be one of the more fuel sensitive versions of this two-cycle

TABLE 15. TEST ENGINE CHARACTERISTICS

Manufacturer	Detroit Diesel	Detroit Diesel	Teledyne Continental	Teledyne Continental*
Designation	6V-53T	3-53	LDT-465-1C	CUE-1790
Induction System	turbocharged	normally aspirated	turbocharged	simulated turbocharge
Combustion System	direct Injection	direct injection	M.A.N.	direct injection
Strokes/Cycle	2	2	4	4
Number of Cylinders	9	3	9	
Arrangement	Λ ,09	in-line	in-line	-
Displacement	5.21L (318 in. ³)	2.61L (159 in. ³)	7,83L (478 in. ³)	2,44L (149.1 in. ³)
Bore and Stroke	9.84 x 11.43 cm (3-7/8x4-1/2in.)	9.84 x 11.43 cm (3-7/8x4-1/21n.)	18.0 x 19.2 (4.56x4.87 in.)	(5.75x5.75 in.)
Rated Power at Speed kW(Hp) at rpm	244(300) at 2800	67.1(90) at 2800	104(140) at 2600	-
Max Torque at Speed	834(615) at 2200	278(205) at 1800	278(205) at 1800 556(410) at 1600	
Compression Ratio	17	21	22	
Fuel System	N70 unit injector	N50 unit injector	Bosch PSB6A-90EH- 5337A3 with ABD-355-124-7 nozzles	

*Single cylinder from Teledyne-Continental AVDS-1790-2D engine adapted to a CUE crankcase by others.

diesel family in the combat fleet. This particular engine powers the M551 tank and the M113 family of armored carriers. The air-cooled AVDS-1790 engine is used in the M60 main battle tank and is vitally important to the military. The Detroit Diesel 3-53 powers the M561 14T vehicle and was used to reduce the fuel consumed in testing, while still giving insight into the performances of these fuels in this family of military two-cycle diesel engines.

The test engines were assembled to the manufacturers' specifications and mounted on appropriate dynamometer test stands. After calibration of the instrumentation, the engines were alternately operated on the test fuels and a petroleum-derived reference fuel. The properties of this reference fuel are given in Table 16. This reference fuel was not intended to represent anything

TABLE 16. PROPERTIES OF REFERENCE 1G/1H DIESEL FUEL

	4.C/m/	
	ASTM	•• •
_	Method	Values
Gravity, °API	D 287	34.4
Density at 15.6°C, g/ml	D 287	0.853
Flash Point, °C	D 93	80
Kin. Viscosity at 38.7°C, cSt	D 445	3.21
Carbon Residue on 10%		
Bottoms, wt%	D 524	0.14
Sulfur, wt%	D 1266	0.399
Cu Strip Corrosion,		
3 hr at 50°C	D 130	la
Neutralization Number,		
mg KOH/g	D 974	0.03
Aromatics, wt% (HPLC)		28
Heat of Combustion, net, Mj/kg	D 240	42.16
Cetane Number	D 613	53
Existent Gum, mg/100 ml	D 381	0
Distillation, °C	D 86	
IBP		194
10%		241
50%		272
90%		316
EP		355
% Recovered		99
% Residue		1
% Loss		ō
/4 2000		•

other than a typical diesel fuel and was chosen because of the control on property repeatability that resulted from its use as the standard fuel for the 1G/1H oil qualification tests. The data generated are reported as observed rather than corrected for ambient conditions, and comparisons to the reference

diesel fuel are made only to the bracketing data points. The resulting performance data are the power produced at full rack (maximum fuel flow) conditions and specific fuel consumption at a fixed power output. The specific fuel consumption is expressed as volumetric consumption, although the consumption was measured gravimetrically. The volumetric fuel consumption at constant power is an indicator of changes in miles per gallon over a fixed operating cycle and is thus an indicator of the additional demands that might be made of the fuel supply logistics system due to changes in fuel composition.

A 210-hour extended duration test was conducted using shale-derived DFM in a Detroit Diesel 3-53 two-cycle engine, a member of the same design family as the 6V-53T. However, this three-cylinder engine was naturally aspirated and configured for military use in the M56l $1\frac{1}{4}$ T military truck.

A. Detroit Diesel 6V-53T Engine

The use of shale JP-5 in the DD6V-53T engine resulted in a 6.0 percent average loss in maximum power output compared to the reference diesel fuel, Table 17 and Figure 15. This result was close to the 6.5 percent power loss observed

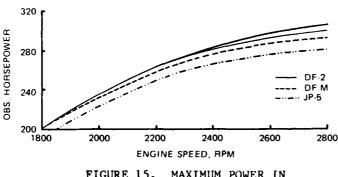


FIGURE 15. MAXIMUM POWER IN DETROIT DIESEL 6V-53T

in the same engine with petroleum-derived JP-5 (<u>18</u>) during earlier test work. Of this 6 percent loss, 4 percent can be attributed to the differences in the net heat of combustion of the two fuels. Another source of maximum power change is leakage of fuel in the injection system. This fuel leakage is

inversely proportional to the fuel viscosity and effectively reduces the fuel delivery rate at fixed rack conditions. This factor accounts for the 2 percent additional power loss observed with the shale JP-5.

This same type of discussion can be applied to the results obtained with the shale DFM fuel. However, the differences in maximum power observed between this fuel and the reference DF-2 fuel were so small that similar differences

TABLE 17. PERCENT CHANGE IN OBSERVED HORSEPOWER IN DETROIT DIESEL 6V-53T

Engine Speed	From DF-2 to DFM	From DF-2 to JP-5
1800	-0.8	-3.4
2000	-1.4	-5.1
2200	-1.8	-5.3
2400	-1.8	-6.2
2600	-1.5	-7.3
2800	-2.4	-8.4
Average	-1.7 ± 0.5	-6.0 ± 0.5

in power output would be expected to occur between fuels which met the DF-2 specifications. This less than 2 percent loss in maximum power would not be expected to be observable under most field conditions.

The change in volumetric fuel consumption at constant power levels was also measured with these two shale-derived fuels. These data, Table 18, are ex-

TABLE 18. PERCENT CHANGE IN VOLUMETRIC FUEL CONSUMPTION IN DETROIT DIESEL 6V-53T BSVC (Gal/BHP-hr), Observed at 100 psi BMEP

Engine Speed	From DF-2 to DFM	From DF-2 to JP-5
1800	1.5	5.8
2000	1.5	4.2
2200	1.1	3.8
2400	1.1	5.5
2600	1.2	5.5
2800	0.9	6.6
Average	1.2 ± 1.0	5.2 ± 1.0

pressed as brake specific volumetric consumption (BSVC) with units of volume consumption rate per unit of work and is an indicator of the relative fuel consumption (as miles per gallon) that would result from a fixed vehicle mission. These data indicate that changing from the reference diesel fuel to the shale JP-5 resulted in a 5.2 percent average increase in BSVC while use of the shale-derived DFM increased BSVC by 1.2 percent. In this mode of operation, injection system leakage is not a factor and only the change in heat content of the delivered fuel must be accounted for. Within the limits of test repeatability and measurement accuracy, the differences in heating value between the fuels are sufficient to explain the measured differences in engine performance.

B. CUE-1790

The CUE-1790 is a cylinder assembly from the Teledyne-Continental AVDS-1790-2D air-cooled diesel engine mounted on a CUE crankcase. The elimination of eleven cylinders necessitated the use of something other than the standard fuel injection system; therefore, American Bosch APE 1BB-1200X4962A injection pump was adapted to this engine when it was originally built. This change in the fuel injection system means that any changes observed in power or fuel consumption when using these fuels in the CUE-1790 cannot be taken to imply that similar results will be obtained in the AVDS-1790-2D engine.

Since the original twelve-cylinder engine is turbocharged, this cylinder assembly is supplied with intake air at elevated temperature and pressure to simulate such operations. Also, a valve is installed in the exhaust duct and the engine back pressure is controlled to the conditions encountered during turbocharging. Because of the differences in engine friction and in the fuel injection system, fuel rates equivalent to the AVDS-1790-2C engine were used to establish the full rack performance level.

The CUE-1790 engine testing was conducted at four conditions listed in Table 19, where the fuel consumption with reference diesel fuel was used to esta-

TABLE 19.	CUE-1790 OPE	CRATING CONDI	TIONS	
Speed, rpm	1800	2000	2200	2400
Fuel Consumption, kg/hr	8.53	9.62	10.66	11.52
Intake Air Temp., °C	87	98	108	116
Intake Air Pressure, kPa	162	182	192	209
Exhaust Pressure, kPa	132	145	159	172
Cooling Air, ΔP , kPa	1.5	1.7	2.0	2.5
Oil Temperature, °C	77	77	77	77
Injection Timing at Ignition, *BTDC	23.8	25.7	25	24.4
Injection Timing at Pump, *BTDC	36	38	38	38

blish a fixed rack setting for evaluating changes in maximum power with the test fuels. The diesel fuel power output level at this condition was also used for the constant power fuel consumption evaluations.

The power results thus obtained, Figure 16 and Table 20, do not agree as closely with the values estimated from the change in fuel heating value and

differences in fixed rack fuel delivery as the data from the DD 6V-53T engine discussed previously. Based on heating value calculations, the shale-derived JP-5 was expected to cause a 4 percent power loss while the shale-derived DFM would be expected to cause no distinguishable change.

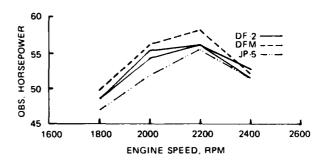


FIGURE 16. POWER AT CONSTANT RACK IN CUE-1790

TABLE 20. PERCENT CHANGE IN OBSERVED POWER IN CUE-1790

Engine Speed, rpm	From DF-2 to DF-M	From DF-2 to JP-5
1800	+2.7	-2.9
2000	+1.4	-4.6
2200	+3.7	-1.1
2400	+1.8	-2.3
Average	+2.4	-2.7
Std Dev	1.0	1.5

Similar results were obtained when evaluating the volumetric fuel consumption at constant power, Table 21. The corresponding calculated change in BSVC based on changes in the fuel heating value indicate a 1 percent increase with DFM and a 4 percent increase with the JP-5. While the JP-5 results agreed closely with the anticipated values, the measured BSVC with the shale DFM showed a slight improvement relative to the calculated results.

TABLE 21. PERCENT CHANGE IN BSVC IN CUE-1790

Engine Speed, rpm	From DF-2 to DFM	From DF-2 to JP-5
1800	-1.1	7.0
2000	-1.4	0.3
2200	-3.0	1.8
2400	-2.9	3.8
Average	-2.1	3.2
Std Dev	1.0	2.9

C. LDT-465-1C

The LDT-465-1C is one member of a family of multifuel engines developed by the military. These engines use the M.A.N. combustion chamber design to obtain improved fuel tolerance and have a fuel injection system which adjusts the full rack fuel delivery as a function of fuel viscosity. As a result of these and other components, these engines can be operated on a variety of fuels ranging from low-octane gasolines through distillate fuels. These engines will typically start and operate with fuel cetane quality as low as 20 without loss in maximum power output.

Due to fuel limitations, the shale-derived JP-5 was not evaluated sufficiently in this engine and only the results obtained with the shale DFM will be discussed here. The data in Table 22 show that as expected from the design, there was no appreciable difference in the maximum power produced with the shale DFM and the reference IG/IH. The difference in volumetric heating value between the two fuels was reflected only as a difference in volumetric fuel consumption, where the shale DFM exhibited a 1.3 percent increase in BSVC.

TABLE 22. PERCENT CHANGE IN OBSERVED POWER AND BSVC IN LDT-465-1C (From 1G/1H Fuel to DFM)

		Change in BSVC, %	
Engine Speed, rpm	Change in Max Power, %	Full Power	3/4 of Full Power
1600	-1.9	+1.3	+0.8
2100	-0.6	-0.1	+1.8
2600	+0.4	+1.0	+2.7
Avg Power Change = Avg BSVC Change = +			

D. 210-Hour Test in Detroit Diesel 3-53 Engine

A 210-hour endurance test was conducted according to the Army/CRC wheeled-vehicle operating cycle using the Detroit Diesel 3-53 two-cycle engine. The shale-derived DFM was used as the fuel, and REO-203 was selected as the lubricant. A summary of the test results is included as Appendix D. There was no power loss during the test nor did after-test inspections reveal any evidence

of distress or impending component failure. The piston deposits and component wear were acceptable. There were no indications of fuel incompatibility or other fuel-related problems.

A similar 210-hour test utilizing a petroleum-derived diesel fuel (19) provided a basis for evaluating the shale fuel results. Averaged over the duration of the tests, and accounting for the less than I percent difference in net heat of combustion, the two fuels were identical in terms of power output at fixed fuel rate and engine thermal efficiency. The endurance test results with the shale-derived DFM are indistinguishable from those obtainable with conventional petroleum-derived diesel fuel with similar properties.

VI. CONCLUSIONS AND RECOMMENDATIONS

The analyses and evaluation of the Paraho-II fuels in the chemical laboratory and in performance tests lead to the following conclusions:

- The JP-8 fuel met all the requirements for Military Specification MIL-T-83133G, Turbine Fuel, Aviation, Kerosene Type, Grade JP-8.
- The JP-5 fuel met all the requirements for Military Specification MIL-T-5624L, Turbine Fuel, Aviation, Grade JP-5, with exception of the requirement of the copper corrosion test and smoke point.
- The DFM fuel met all the requirements of Military Specification MIL-16884G, Amendment I, Fuel Oil, Diesel, Marine, with the exception of the requirement for cloud point.
- Investigation of the compatibility of Paraho-II fuels, JP-5, and DFM,
 with petroleum-based fuels resulted in no incompatibility under the conditions studied.
- Storage tests at 80°C indicated that both JP-5 and DFM produced from the Paraho-II shale oil are relatively unstable at this temperature compared to petroleum-based fuels.

- Paraho-II shale-derived fuels responded to treatment with cetane improver additive similarly to a petroleum-based fuel.
- The JP-5 and DFM shale fuels performed poorly with respect to protecting a steel surface against corrosion, as indicated by the NACE corrosion test. A commercial additive package containing a corrosion inhibitor, improved this performance parameter only incrementally.
- Microbiological growth susceptibility investigations resulted in heavy growth of <u>Cladosporium resinae</u> in the shale fuels between the second and third month of incubation.

Gas turbine combustion performance evaluation of the shale-derived JP-5 and DFM fuels resulted in the following conclusions:

- The combustion performance characteristics of the syncrude JP-5 and DFM test fuels did not deviate significantly from the petroleum-derived Jet A reference fuel.
- Slight differences in combustion efficiency were observed at the lower power points; DFM burned with somewhat lower efficiency than JP-5 and the reference fuel, Jet A.
- The carbon monoxide emissions followed the same trend as combustion efficiency. At the lower power points, DFM showed slightly higher CO than JP-5 and Jet A.
- \bullet There were no fuel property effects on the emissions of unburned hydrocarbons and NO $_{_{\mathbf{Y}}}\bullet$
- The flame radiation and exhaust smoke levels for the synfuels were higher than those of Jet A. This is attributed to differences in hydrogen content. The DFM fuel correlated with hydrogen content in the same way as petroleum-derived fuels; JP-5 from shale oil gave higher than expected radiation and smoke.

From the evaluation of Paraho-II JP-5 and DFM in diesel engines, the following conclusions were deduced:

- The shale JP-5 in the DD6V-53T engine showed a 6 percent average loss in maximum power output when compared to the reference diesel fuel. This approximates the 6.5 percent power loss observed in the same engine with petroleum-derived JP-5.
- Only slight differences in maximum power output were observed between the shale DFM and petroleum DF-2.
- The shale-derived JP-5 and DFM performed in the CUE-1790 engine as might be expected from the similar petroleum-derived fuels. There was a slight improvement in BSVC with the DFM which within the context of the other test results appears to be an anomaly.
- Evaluation of DFM from shale in the LDT-465-1C engine resulted in no difference between the maximum power produced by this fuel and that of a petroleum No. 2 diesel fuel; however, a difference in volumetric fuel consumption observed was attributed to the difference in volumetric heating values between the two fuels.
- The results from the 210-hour test in the DD 3-53 engine are indistinguishable from those that may result from tests with conventional petroleum-derived diesel fuel with similar properties.

The results of the program suggest that additional work should be conducted in certain areas; thus, it is recommended that:

- The Paraho-II shale fuels should be further evaluated for additive response to corrosion inhibitors.
- Other finished synthetic fuels, shale- or coal-derived, that may become available in adequate quantities should be evaluated extensively as these fuels have been.

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APPENDIX A STORAGE STABILITY TEST AT 43° C

Summary

The storage stability test at 43°C is intended to accelerate the deterioration process that may occur in fuels stored for periods of one year and over. The storage stability characteristics of fuels can be estimated by this technique.

Aliquots of test fuels are placed in a series of clean liter or other size bottles which are then placed in storage at 43° ± 3°C. After 4, 8, 16, and 32 weeks, pairs of bottles are removed from storage, filtered for determination of precipitate formed during storage; the bottles are rinsed with triple solvent and the insoluble or adherent gum is measured; and the filtered fuel is measured for existent gum.

Cleaning the Storage Bottles

- 1. Scrub with a detergent solution and rinse with water.
- Fill the bottle about half full with chromic acid cleaning solution, roll the bottle for complete contact of acid with the inner surface, pour out the acid, and allow the bottle to stand for at least 1 hour.
- 3. Rinse with tapwater, then invert and flush with a stream of distilled water.
- 4. Allow the bottle to drain. Dry overnight in a 150°C oven.

Aging at 43°C

Filter the fuel through a membrane filter having 0.45-micron pore size to remove particles. Place 280 ml of fuel in each of ten 32 oz (946 ml), screw cap, amber bottles. Seal with screw caps lined with Teflon. Store in the dark at a constant temperature of 43°C. After each storage interval--4, 8, 16, and 32 weeks from the beginning of storage--remove two samples and analyze for gum. Use two samples as "floaters" for additional analysis at unscheduled times. Every four weeks, during the storage, replenish the oxygen in the vapor space. To do this, remove all bottles, cool, aerate, and return to storage.

Aerating Storage Samples

- 1. Remove the sample from 43°C storage and cool to 0-4.5° overnight.
- 2. Remove the bottle caps for five minutes.
- 3. Recap the sample; when the sample has warmed to room temperature, return it to 43°C storage.

Analyzing Storage Samples

The fuel-insoluble gum and the precipitate are separated from the fuel by filtration. Soluble gum is determined on the filtered fuel as is "unwashed" gum by ASTM Method D 381. Insoluble gum is dissolved in organic solvents and weighed after evaporation of solvent. Precipitate is determined by weighing the filter.

Materials and Apparatus

Glass reservoir, with air pressure connection and an approximately 9-mm-OD delivery tube.

Size 9 neoprene stopper, bored to accept delivery tube.

Gooch low-form filtering crucible: Pyrex, fritted disk, 30 ml, fine porosity.

Crucible holder.

Eight ASTM D 381 air-jet gum beakers.

Two graduated bottles, at least 12 oz (355 ml).

Stirring rod with policeman.

Gum solvent (1:1:1 acetone-toluene-methanol).

n-Heptane.

D 381 gum bath; analytical balance; 93°C oven; covered container for beakers and filter.

Determining Soluble Gum

Weigh a filtering crucible (hereafter called "filter") and eight gum beakers. Assemble the reservoir-stopper-filter-holder arrangement for filtration, as shown in Figure A-1. With gentle air pressure, pass the aged fuel from bottle A through the filter and collect the filtrate in a graduated bottle. Set aside. Pass the fuel from bottle B through the same filter, collecting in a separate bottle. Measure two 50 ml portions of the filtrate from bottle A, and from bottle B into gum beakers. Determine air-jet gum on each by ASTM Method D 381. Average the results and report as soluble gum, in mg/100 ml.

Determining Insoluble Gum

Place a container beneath the filter. Rinse each bottle and the filter free of fuel by adding three successive 50-ml portions of heptane into each bottle by gentling swirling, and pass rinsings through filter. Discard rinsings.

Place a weighed gum beaker beneath the filter. Rinse and police bottle A with 15 ml of gum solvent, then pass the solution through filter into beaker. Repeat twice with 15- to 20-ml portions of solvent for a total of not more than 50 ml of solution in gum beaker.

Place another gum beaker beneath filter and carry out the gum solvent steps on bottle B.

Evaporate solvent from the two solutions by the air-jet method described in ASTM D 381 and weigh the residues.

Insoluble gum, mg/100 ml =
$$\frac{\text{residue A, mg + residue B, mg}}{5.6}$$

This number represents the combined filtered volume of fuel from bottles A and B divided by 100. If the total volume differs from 560 ml, this denominator should be changed accordingly.

To obtain total gum, add the insoluble gum and soluble gum values.

Determining Precipitate

To determine the precipitate collected on the filter, dry the filter in a 93°C oven for 1 hour, cool at least 2 hours, and weigh.

Precipitate, mg/100 ml =
$$\frac{\text{precipitate, mg}}{5.6}$$

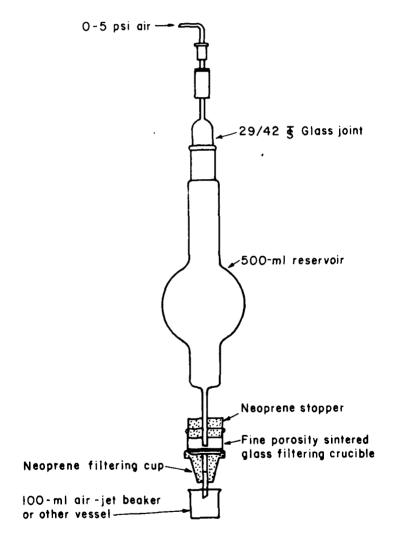


FIGURE A-1. FILTERING ASSEMBLY

APPENDIX B

PROTON NMR SPECTRA

Proton NMR spectra measured on 90-MHz NMR Spectrophotometer, by technique described by Myers, et al.

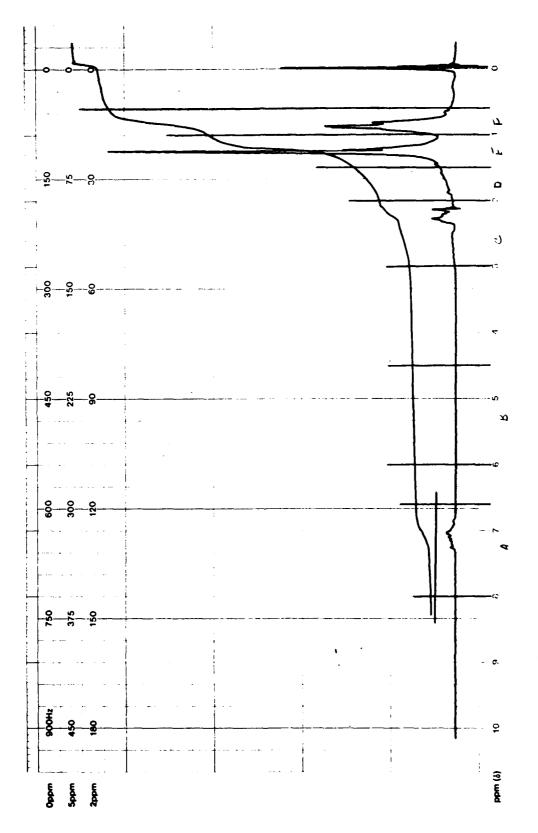


FIGURE B-1. JP-8 AIRCRAFT TURBINE FUEL FROM SHALE OIL

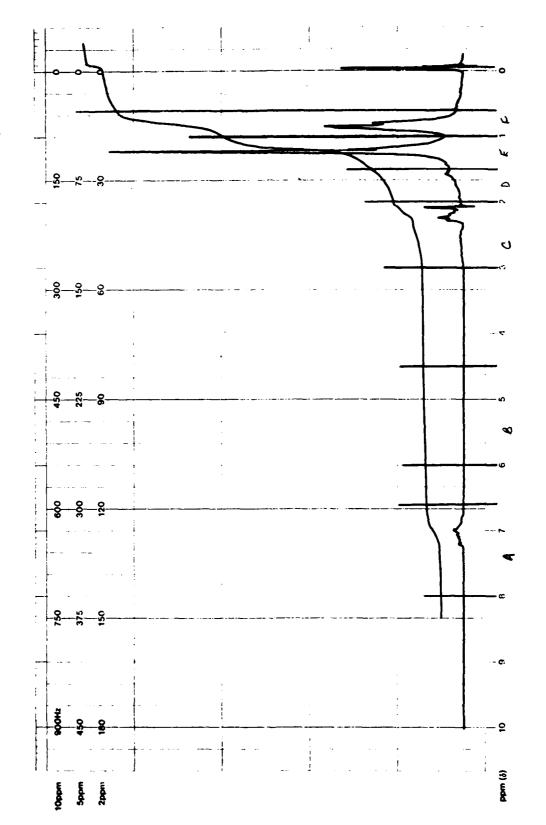


FIGURE B- 2. JP-8 AIRCRAFT TURBINE FUEL FROM SHALE OIL AFTER 32 WEEKS IN 43°C STORAGE

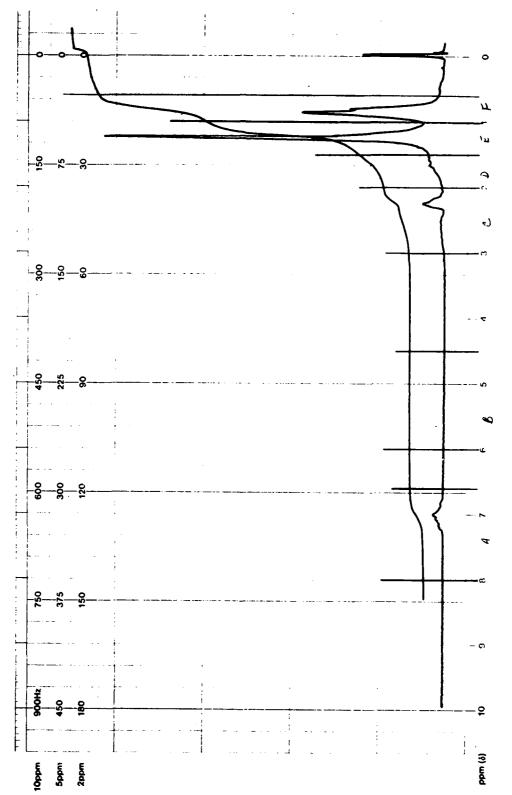


FIGURE B-3. JP-5 AIRCRAFT THAINE FUEL FROM SHALE OIL

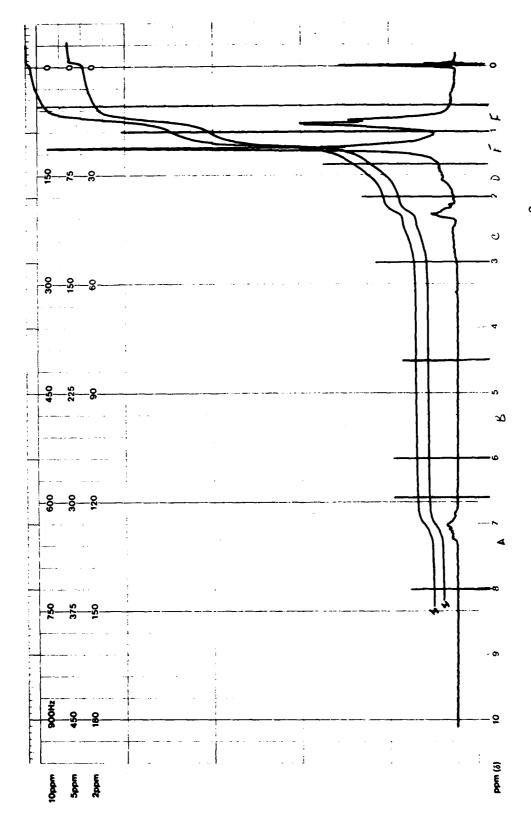


FIGURE B-4. JP-5 AIRCRAFT TURBINE FUEL FROM SHALE OIL AFTER 32 WEEKS IN 43°C STORAGE

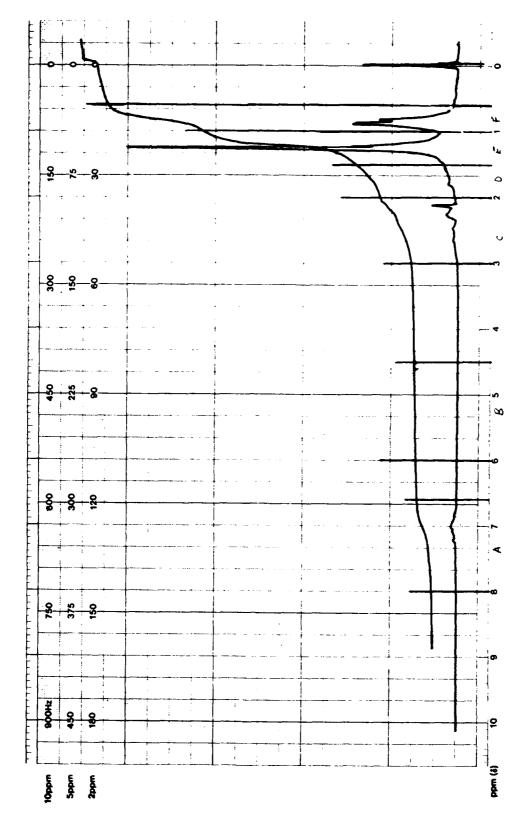
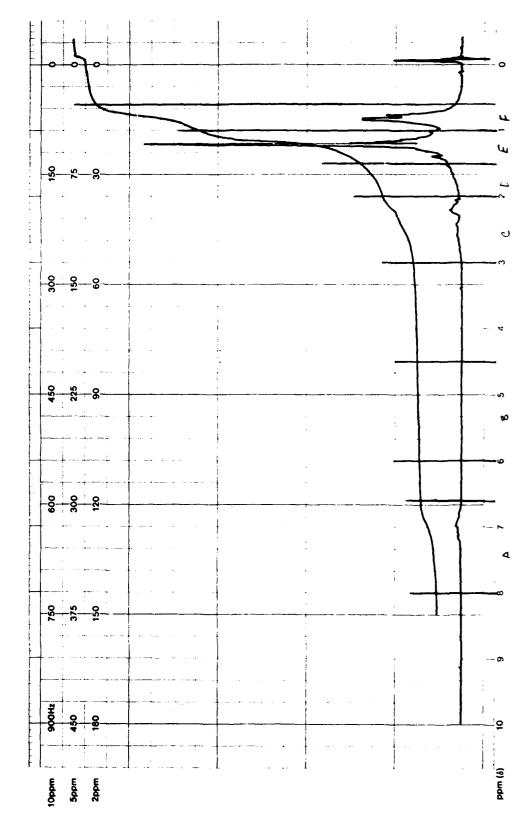


FIGURE B-5. MARINE DIESEL FUEL FROM SHALE OIL



MARINE DIESEL FUEL FROM SHALE OIL AFTER 32 WEEKS IN 43°C STORAGE FIGURE B-6.

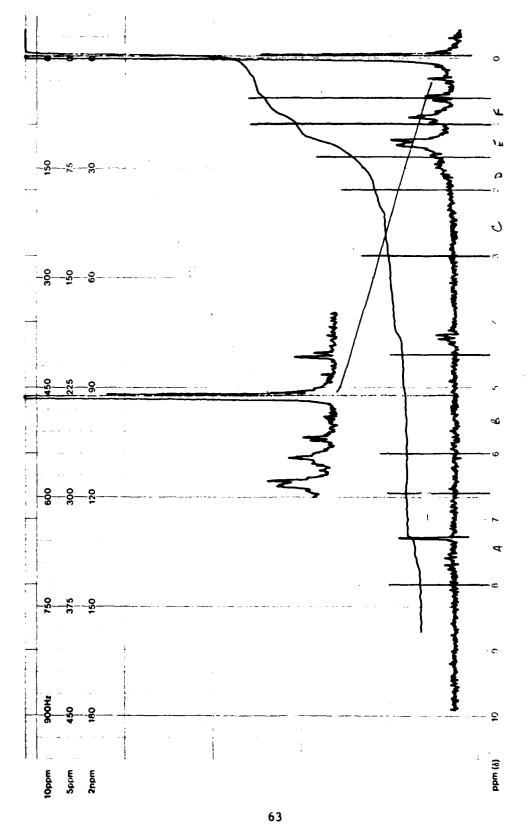


FIGURE B-7. FUEL-SOLUBLE GUM FROM SHALE-DERIVED JP-8 AFTER 32 WEEKS IN 43°C STORAGE

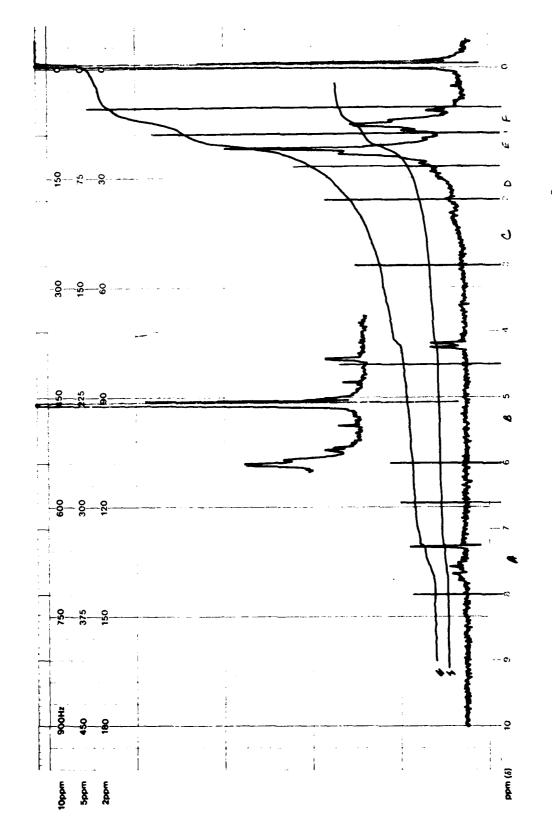


FIGURE B-8. FUEL-INSOLUBLE GUM FROM SHALE-DERIVED JP-8 AFTER 32 WEEKS IN 43°C STORAGE

APPENDIX C

13_{C NMR} SPECTRA

C NMR Spectra measured on a CFT-20, Fourier Transform NMR instrument operating at 20-MHz. Method 4, as described by Shoolery and Budde(8), was employed for these measurements.

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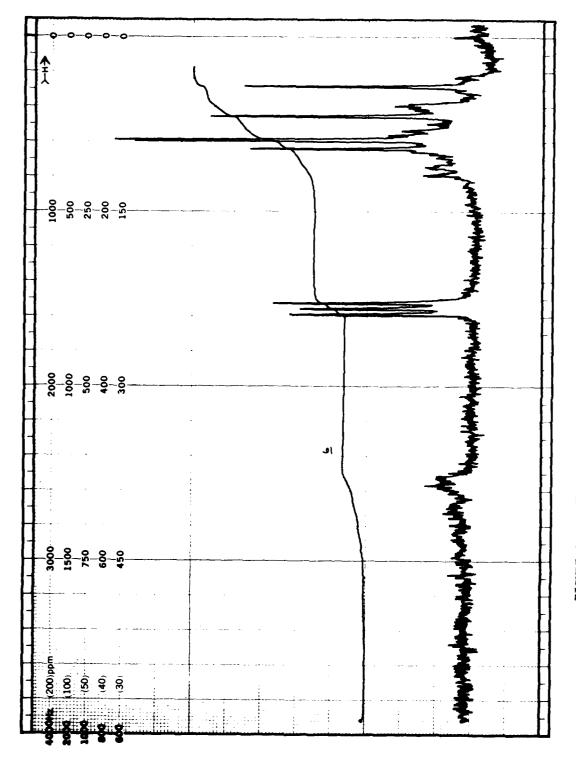


FIGURE C-1. JP-8 AIRCRAFT TURBINE FUEL FROM SHALE OIL

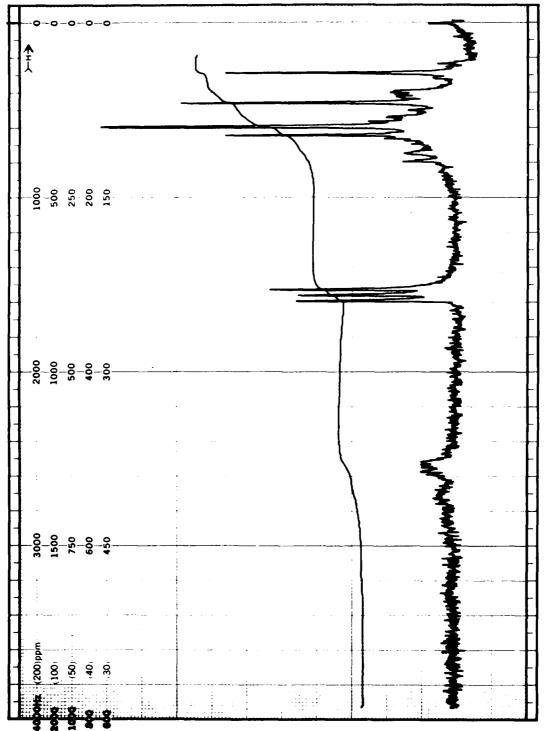


FIGURE C- 2. JP-8 AIRCRAFT TURBINE FUEL FROM SHALE OIL AFTER 32 WEEKS IN 43 °C STORAGE

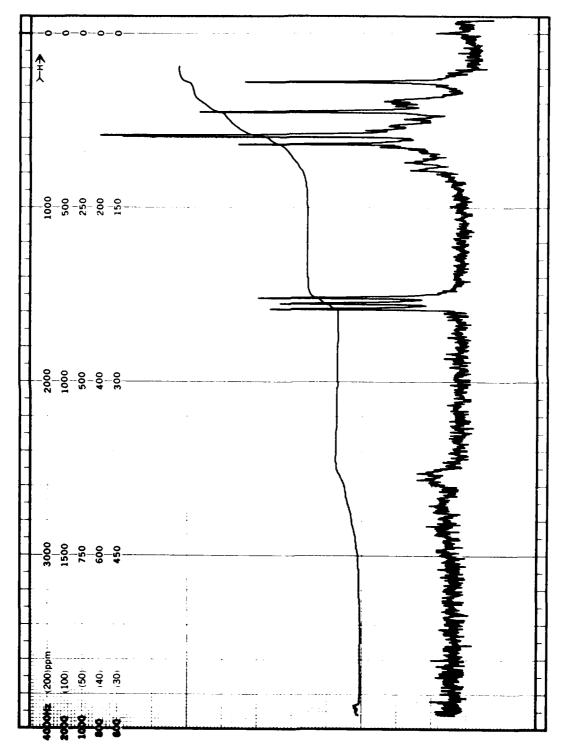


FIGURE C- 3. JP-5 AIRCRAFT TURBINE FUEL FROM SHALE OIL

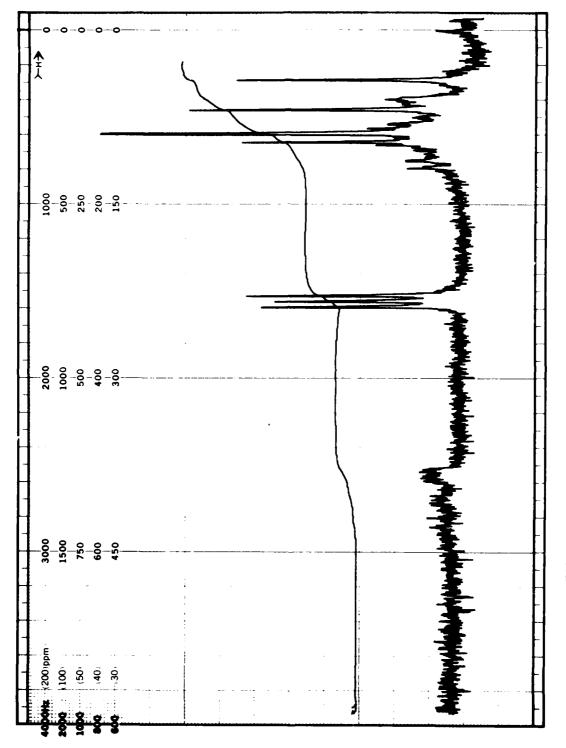


FIGURE C- 4. JP-5 AIRCRAFT TURBINE FUEL FROM SHALE OIL AFTER 32 WEEKS IN 43°C STORAGE

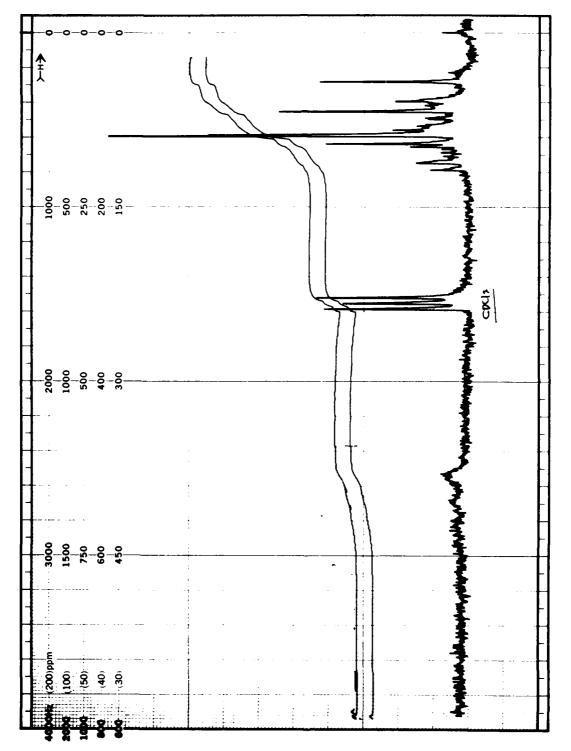


FIGURE C- 5. MARINE DIESEL FUEL FROM SHALE OIL

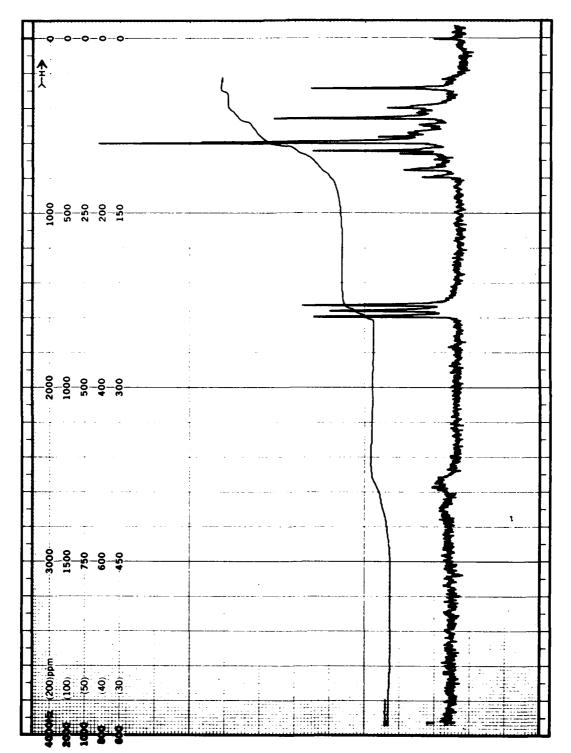


FIGURE C- 6. MARINE DIESEL FUEL FROM SHALE OIL AFTER 32 WEEKS IN 43°C STORAGE

APPENDIX D

ENGINE-FUEL COMPATIBILITY TEST 210-HOUR WHEELED-VEHICLE CYCLE USING 3-53 DIESEL ENGINE ENGINE-FUEL COMPATIBILITY TEST 210 HOUR WHEELED VEHICLE CYCLE USING 3-53 DIESEL ENGINE

Test Fuel: Paraho Shale DFM, AL-8437-F Test Lubricant: REO-203, AL-8822-L Date Completed: 21 April 1980

Conducted for

U.S. Army Mobility Equipment Research and Development Command Energy and Water Resources Laboratory Ft. Belvoir, Virginia

bу

U.S. Army Fuels and Lubricants Research Laboratory Southwest Research Institute San Antonio, Texas

PRECEDING PACE BLANK-NOT FILIED

ENGINE OPERATING DATA (AVG) SHALE DF-M TEST

		Power		Idle
	Min	Max	Avg	(Avg)
Engine Speed, rpm	2790	2814	2801	649
Load, 1b	103	112	109	
Torque, 1b-ft	180	196	191	
BHp obs	96	105	102	
Fuel Rate, 1b/hr	42.6	45.0	44.0	
BMEP, psi	85	93	91	
BSFC 1b/BHp-hr	.413	.450	.430	
Temperatures, °F				
Jacket Coolant-In	194	199	197	97
Jacket Coolant-Out	201	205	204	102
Oil Sump	242	255	253	
Inlet Air (Blower)	70	104	82	
Exhaust Manifold	920	1015	972	
Fuel @ Return	134	150	140	
Fuel @ Filter	80	101	90	
Pressures				
Oil Gallery, psig	44	46	45	
Blower Discharge, psig	4.5	5.0	4.7	
Intake Vacuum, in. H ₂ O	6.5	7.0	6.9	
Crankcase, in. H ₂ O	52	66	60	
Exhaust, Common, in. Hg	1.9	2.8	2.3	
Transfer Pump, psig	74	76	76	
Oil Consumption, lb/hr			0.25	

AL-8822-L LUBRICANT ANALYSES SHALE DF-M TEST

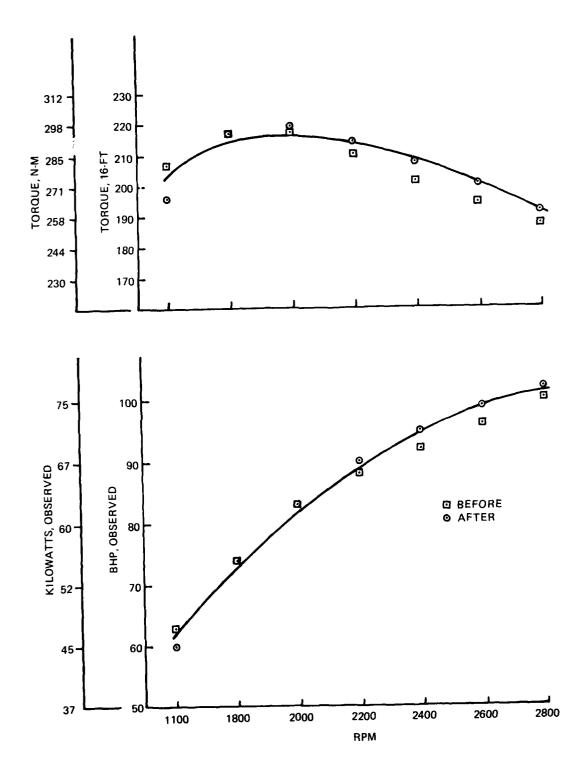
		New	70	140	210
Property	Method	0i1	Hrs	Hrs	Hrs
K. Vis, cS, 40°C	D445	104.6	114.9	124.0	129.2
K. Vis, cS, 100°C	D445	11.8	12.8	13.5	14.1
VI	D2270	101	104	105	107
TAN	D664	3.6	3.35	3.62	3.68
TBN	D2896	5.4	2.82	3.24	2.82
Insolubles, wt%	D893			3.2.	2.02
Pentane A		0.0	ND	ND	0.06
Toluene A		0.0	ND	ND	0.05
Pentane B		0.0	ND	ND	0.95
Toluene B		0.0	ND	ND	0.84
API Gravity, °	D287	27.0	27.0	26.8	26.3
Pour Point, °C (°F)	D92	-21(-6)	-21(-6)	-21(-6)	-21(-6)
Carbon Residue, wt%	D524	1.19	1.68	1.96	2.27
Sulfated Ash, wt%	D874	0.93	1.15	1.26	1.34
Elemental	Method		-		
Ca, wt%	AA	0.24	0.31	0.34	0.36
Zn, wt%	AA	0.09	0.13	0.14	0.15
Cu, ppm	AA	-	3	4	4
Cr, ppm	AA	-	<1	<1	< i
Pb, ppm	AA	-	7	7	8
Fe, ppm	AA	-	25	42	53

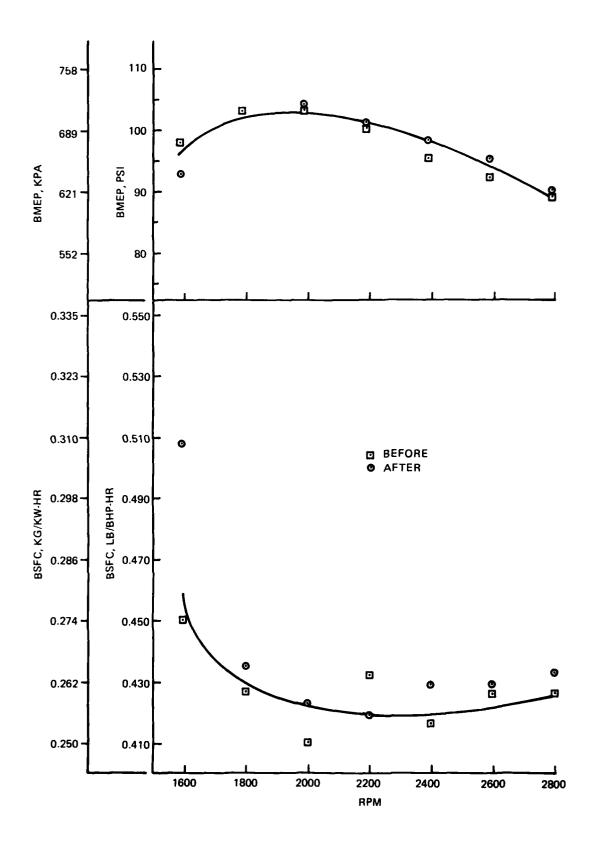
ND = Not Determined AA = Atomic Absorption

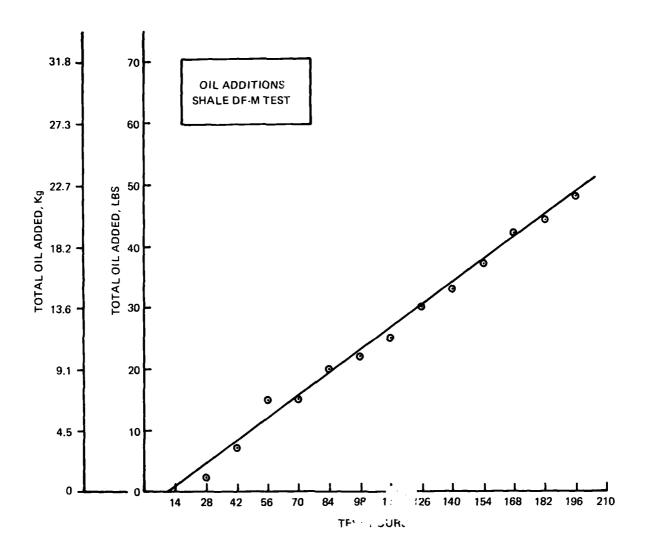
XRF = X-Ray Fluorescence

DAILY WEAR METALS BY XRF SHALE DF-M TEST

Test	Iron	Other Wear
Hours	ppm	Elements
14	27	None detected
28	33	None detected
42	30	None detected
56	38	None detected
70	47	None detected
84	43	None detected
98	59	None detected
112	60	None detected
126	63	None detected
140	68	None detected
154	60	None detected
168	80	None detected
182	74	None detected
196	75	None detected
210	85	None detected







RING FACE CONDITION: % BURNING SHALE DF-M TEST

	Cylinder Number		
	1	2	3
First Ring	5	15	20
Second Ring	N	85	55
Third Ring	N	75	55
Fourth Ring	N	50	60
Average of all	1	56	48
Average of all	1	50	46

N = Normal

RING STICKING SHALE DF-M TEST

Ring		Piston Number			
Ring No.	1	2	3		
1	5% P	20% P	50% P		
2	F	F	F		
3	F	F	F		
4	F	F	F		

F = Free

P = Pinched

CYLINDER LINERS SHALE DF-M TEST

Cylinder Liner Scuffing Percent of Compression Ring Travel Area

			ITAVEL A	rea		
Cylinder Number	Percent Port Restriction		ent Scuffed Anti-Thrust	<pre>% Total Area Scuffed</pre>	% Glazed	% Lacquer
1	5	5	10	8	15	85
2	2	5	90	48	10	90
3	1	1	35	18	10	90
Average	3	4	45	24	12	88

PISTON O.D. (IN) SHALE DF-M TEST

Cylinder	1	2	3
Before After	3.8709 3.8699	3.8709 3.8700	3.8708 3.8699
Change	0.0010	0.0009	0.0009

PISTON SURFACE CONDITION SHALE DF-M TEST

	Piston Number			
	1	2	3	
Top Land Skirt Piston Pin	N Lt. Scratches N	N Lt. Scratches N	N Lt. Scratch s	

PISTON GROOVE INSIDE DIAMETER % RING SUPPORTING CARBON SHALE DF-M TEST

D1-4 D1			er	
Piston Ring	Quadrant	1	2	3
1	1	0	95	95
	2	0	0	0
	3	0	0	0
	4	0	0	0
2	1	0	10	0
	2	0	0	5
	3	85	95	90
	4	0	15	5

Quadrants:

I = Thrust

2 = Rear

3 = Anti-thrust

4 = Front

EXHAUST VALVE DEPOSITS SHALE DF-M TEST

		Cylinder Number				
<u>Area</u>	11	2	3			
Head	10% BHC	40% AHC	50% ¹ ₂AHC			
Face	~~~~~~~~	AHC to #9 Lacquer				
Tulip		AHC to #9 Lacquer				
Stem		#9 Lacquer to Clean	n			

EXHAUST VALVE SURFACE CONDITIONS SHALE DF-M TEST

	Cylinder Number			
	1	2	3	
Freeness in Guide	F	F	F	
Head	N	N	N	
Face	Some	light leaking due to	deposits	
Seat	N	N	N	
Stem	N	N	N	
Tip	N	N	N	

F = Free

N = Normal

RING DEPOSITS SHALE DF-M TEST

CRC DIESEL RATING SYSTEM

278.75 NO. 1 GROOVE, VOLUME % PISTON WTD. RATING PISTON NO. _ LANDS STANDARD COMPUTATION SHEET FOR PISTON RATING LABORATORY TEST NUMBER Shale DF-M STAND NO 2 ENGINE NO 3D-131703 TEST PROCEDURE Wheeled Vehicle TEST LABORATORY AFLRL LUBRICANT AL-8822-L 210 TEST HOURS_

					GROOVES	VES		,	1		ļ.	!	4	LANDS				UNDER	É
DEPOSIT		Š	1 .	ž	NO. 2	Ž	NO. 3	NO. 4	4	NO. 1		S	NO. 2	ž	NO. 3	NO.	+	CROWN	₹
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Š	8.	10	10.00	30	30.00			10	10.00	15	15.00	15	15.00						
ž	MHC 0.75					15	11.25												
NO NO	0.50	20	35.00	10	5.00			5	2.50	85	42.50	20	10.00						
887 5	c 0.25	20	5.00	09	15.00	10	2.50	5	1.25			40	10.00	50	12.50	25	6.25		
	VLC 0.15					75	11.25					25	3,75			15	2.25		
<u> </u>	CARBON	<i>U</i> 1	50.00	<i></i>	50.00	25	25.00	13	13.75	57	57.50	38	38.75	12	12.50	8.50	0		
BL	L 0.100													50	5.00			100	10.00
8	DBrL 0.075							80	6.00										
R A	0.050															10	.50	1	
4 30E	ער 0.025															50	1.25	1	
)SA }	AL 0.010																		
7	RL 0.001																		
	LACQUER							9	6.00					5.	5.00	1.75		10.00	8
CLEAN	0																	7	
102	ZONAL RATING																		
100	LOCATION FACTOR							Li				1	!						
¥E.G	WEIGHTED RATING	50.00	00	~	50.00	25	25.00	19	19.75	57.50	50	38	38.75		17.50	10.25	25	10.00	8

CRC DIESEL RATING SYSTEM

STANDARD COMPUTATION SHEET FOR PISTON RATING RATER E. Lyons
LABORATORY TEST NUMBER Shale DF-M
STAND NO. 2 ENGINE NO. 3D-131703
FUEL AL-8437-F TEST PROCEDURE Wheeled Vehicle TEST HOURS 210
TEST LABORATORY AFTRL
LUBRICANT AL-8822-L

NO. 1 GROOVE, VOLUME-%

PISTON NO.

DATE 4-23-80

TYPE TYPE HC HC MHC																			
NO8					GROOVES	OVES	i			-		i	د	LANDS					1
Y Z Z	FACTOR	2	-	NO	5.2	ž	NO. 3	Ş	NO. 4	NO.		S	NO. 2	Ž	NO. J	Ž	Q C	5 8	CROWN
¥ ₹ ¥		AREA-%	AREA-% DEMERIT AREA-%	AREA %	DEMERIT	AREA.%	DEMERITAREA'S DEMERIT		DEMERIT	AREA-%	AREA % DEMERIT AREA % DEMERIT AREA % DEMERIT AREA % DEMERIT	AREA.%	DEMERIT	AREA-%	DEMERIT	ARFAK	AREA. WINDERPLIT AREA WINDERS	ABCAK	DEMES
¥ ĕ SON	1.00	20	20.00	65	65.00					75	75.00	06	00 06						0.0
	IC 0.75																		
	0.50	10	5.00	25	12.50					20	10.00			5.5	27.50				
7 L	0.25	70	17.50	10	2.50	50	12.50	2	1.25	5	1.25	2	2.50	2 5	5.00				
ט ארכ	C 0.15					50	7.50					2		25	27.5				
	CARBON	42	42.50	8	00.00		20.00] -	1.25	98	86.25	92	92.50		36.25				
B	0.100															: ا			
DBrL	יר 0.075															2	1.50	3	10.00
A:	0.050							5	-										
₹ N	L 0.025							75	1 875							1			
₹	JL 0.010															<u>د</u>	2.125		
7	0.001																		
	LACQUER							2.875	7.5							7	3715	2	
CLEAN	0																Ç	10.00	
/NO2	ZONAL RATING											1							
LOCATI	LOCATION FACTOR																		
WEIGHI	WEIGHTED RATING	42.50	20	8	00	20.00	00	3.900	00	86	86.75	92 00	1 0	36 75	35		,		

CRC DIESEL RATING SYSTEM

STANDARD COMPUTATION SHEET FOR PISTON RATING

TEST PROCEDURE Wheeled Vehicle TEST LABORATORY AFLRE LUBRICANT AL-8822-L TEST HOURS

PISTON NO.

NO. 1 GROOVE, VOLUME % PISTON WTD. RATING LABORATORY TEST NUMBER Shale DF-M STAND NO 2 ENGINE NO 3D-131703 FUEL AL-8437-F

312.00

AREAS DEMENTAREAS DEMENTAREAS DEMENT AREAS DEMENTAREAS DEMENTAREAS DEMENTAREAS DEMENTAREAS DEMENTAREAS DEMENTA 10.00 UNDER. CROWN 10.00 10.00 100 13.75 .50 1.50 .50 21.25 **N**0 1.50 19.75 10 10 75 6.75 25.00 . 25 31.75 32.00 NO.3 .25 LANDS 20 45 50.00 12.50 62.50 NO. 2 62.50 20 50 40.00 15.00 55.00 55.00 ~ 0 07 09 2.50 NO. 4 2.50 2.50 100 8.75 3.00 4.50 11.75 16.25 NO 3 4.50 GROOVES 20 35 15.00 40 40.00 55.00 55.00 NO. 2 9 12.50 40.00 5.00 57.50 57.50 N 0 40 20 20 LOCATION FACTOR WEIGHTED RATING OEPOSIT FACTOR 0.010 0.050 0.025 0.00 DB1L 0.075 BL 0.100 8 0.75 0.50 **ZONAL RATING** 0.25 VLC 0.15 LACQUER CARBON RATING 0 TACQUER MHC DEPOSIT TYPE S ٦ υ Σ CLEAN ٩٢ CARBON

*WEIGHTED TOTAL DEPOSITS

CYLINDER LINER I.D. (IN) SHALE DF-M TEST

		Front/Bac	k	Thr	ust/Antit	hrust
Cylinder	Par	allel to	Crank	<u>Perpen</u>	dicular t	o Crank
Number	Top	Middle	Bottom	Тор	Middle	Bottom
1. After	3.8776	3.8774	3.8770	3.8784	3.8779	3.8772
Before	3.8772	3.8769	3.8767	3.8774	3.8770	3.8765
Change	0.0004	0.0005	0.0003	0.0010	0.0009	0.0007
2. After	3.8772	3.8775	3.8773	3.8787	3.8778	3.8771
Before	3.8763	3.8769	3.8769	3.8773	3.8771	3.8768
Change	0.0009	0.0006	0.0004	0.0014	0.0007	0.0003
3. After	3.8774	3.8775	3.8769	3.8779	3.8780	3.8775
Before	3.8771	3.8771	3.8769	3.8769	3.8773	3.8771
Change	0.0003	0.0004	0.0000	0.0010	0.0007	0.0004
Average (All)	0.0006					
Average T/AT	0.0008					

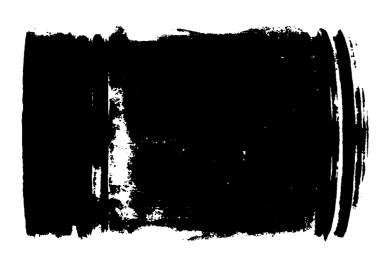
PISTON RING GAP (IN) SHALE DF-M TEST

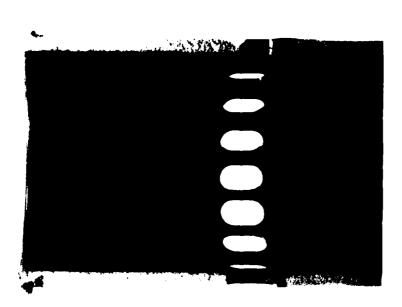
				Ring	Number			
Piston Number	1	2	3	4	5	6	7	8
l. After	0.035	0.029	0.028	0.029	NM	NM	NM	NM
Before	0.032	0.028	0.028	0.029	0.022	0.022	0.022	0.022
Change	0.003	0.001	0.000	0.000	-	-	-	-
2. After	0.036	0.028	0.028	0.029	NM	NM	NM	NM
Before	0.035	0.028	0.028	0.029	0.020	0.020	0.020	0.019
Change	0.001	0.000	0.000	0.000	-	-	-	-
3. After	0.037	0.032	0.030	0.032	NM	NM	NM	NM
Before	0.034	0.032	0.029	0.031	0.020	0.020	0.019	0.021
Change	0.003	0.000	0.001	0.001	-	-	-	-

Avg F/R (#1) Wear 0.002

NM = Not Measured

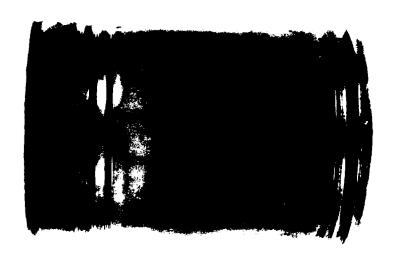
PISTON AND CYLINDER LINER CONDITION SHALE DF-M TEST

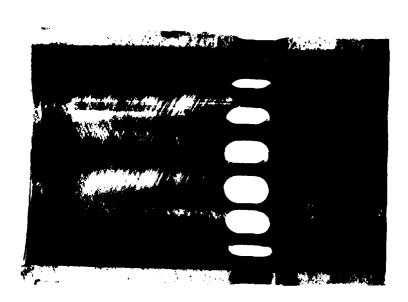




No. 2 - Antithrust Side (worst)

PISTON AND CYLINDER LINER CONDITION SHALE DF-M TEST





No. 3 Thrust Side (best)

RING FACE CONDITION SHALE DF-M TEST



Piston - 1



Piston - 2



Piston - 3

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FORT BENNING GA 31905		CODE 6180	Ī
TORT BERNIERO ON 31903		CODE 6110 (DR HARVEY)	1
CDB		WASHINGTON DC 20375	1
CDR		WASHINGTON DC 20373	
US ARMY AVIATION CTR & FT RUCKER		ann.	
ATTN ATZQ-D	1	CDR	
FORT RUCKER AL 36362		NAVAL FACILITIES ENGR CTR	
		ATTN CODE 1202B (MR R BURRIS)	1
DEPARTMENT OF THE NAVY		CODE 120B (MR BUSCHELMAN)	1
		200 STOVALL ST	
CDR		ALEXANDRIA VA 22322	
NAVAL AIR PROPULSION CENTER			
ATTN PE-71	1	CHIEF OF NAVAL RESEARCH	
PE-72 (MR D'ORAZIO)	1	ATTN CODE 473 (DR R MILLER)	1
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CODE 6101F (MR R LAYNE)	1	LAKEHURST NJ 08733	
WASHINGTON DC 20362			
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CDR		NAVY FACILITIES ENGRG CMD	
DAVID TAYLOR NAVAL SHIP R&D CTR		CIVIL ENGR SUPPORT OFC	
CODE 2830 (MR G BOSMAJIAN)	1		1
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ANNAPOLIS MD 21402		FORT HUENEME CA 93043	
		ODD MANAL MAMERIAL COLOMB	
JOINT OIL ANALYSIS PROGRAM -		CDR, NAVAL MATERIAL COMMAND	
TECHNICAL SUPPORT CTR	1		1
BLDG 780		CP6, RM 606	
NAVAL AIR STATION		WASHINGTON DC 20360	
PENSACOLA FL 32508			
		CDR	
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HQ, US MARINE CORPS		ATTN CODE 40	1
ATTN LPP (MAJ SANBERG)	1	CAMERON STATION	-
LMM (MAJ GRIGGS)	1	ALEXANDRIA VA 22314	
	1	ADDARHUKIA VA 22314	
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		CDR	
CDR		MARINE CORPS LOGISTICS SUPPORT	
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NAVAL AIR DEVELOPMENT CTR		HQ, USAF	
ATTN CODE 60612 (MR L STALLINGS)	1	ATTN RDPT	ı
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